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Development of exopolysaccharide membranes for dehydration processes

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Development of exopolysaccharide membranes for dehydration processes

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ABSTRACT

This PhD work proposes the use of two microbial exopolysaccharides, GalactoPol and FucoPol, for the development of membranes to be applied in relevant dehydration processes in industry. The starting material is obtained from a low cost, abundant carbon source, the glycerol produced as a by-product from the biodiesel industry, which represents a key economic advantage.

A special attention was given to the development of membranes with enhanced mechanical and transport properties, and superior water selectivity for application in dehydration processes by pervaporation and vapour permeation. The approaches selected for designing target membrane properties included polymer cross-linking and the development of hybrid membranes using the sol-gel method.

Firstly, the membranes were modified using different crosslinking agents: trichloroacetic acid for GalactoPol and genipin for Fucopol. Different crosslinking protocols were studied in order to evaluate their potential use for ethanol dehydration by pervaporation. These membranes were characterised in terms of their morphological structure, resistance to solvents and mechanical properties. They showed high water affinity, good chemical resistance towards organic solvents and adequate mechanical properties. Pervaporation experiments were performed using both types of membranes for different water concentration in the feed stream (5.0 to 10.0 wt.%) at a constant temperature of 30 ºC.

In addition, the impact of the exopolysaccharide purification protocol – by dialysis and by-dia-ultrafiltration – on the properties and transport performance of composite FucoPol membranes for pervaporation was also studied. Significant differences were found in the swelling behaviour and transport selectivity depending on the purification method. The shear stress imposed during purification by the dia-ultrafiltration method led to a disintegration of polysaccharide aggregates, and, as consequence, denser membranes were obtained, affecting the transport selectivity. The membranes developed, in particular, the composite GalactoPol-PES and dia-ultrafiltrated FucoPol-PES membrane, exhibited a high potential for ethanol dehydration, since a water/ethanol selectivity of 134 and 143, respectively, at 10.0 wt.% water in ethanol was achieved.

Although they showed excellent affinity for water, they become progressively unstable in aqueous solutions. Thus, novel hybrid FucoPol membranes were developed combining the best properties of the inorganic network with the selectivity of the microbial polysaccharides, to be applied in pervaporation processes for ethanol dehydration, as well as, in gas dehydration. The hybrid membranes were prepared by incorporation of a SiO_2 network homogeneously dispersed by a sol-gel method using (3-Glycidyloxypropyl) trimethoxysilane (GPTMS) as a crosslinker silica precursor. These membranes were structurally, mechanically and thermally characterised. They presented a dense and homogeneous structure, resistant to deformation, a glass transition temperature (Tg) of 43 ºC and a thermal decomposition between 240-251 ºC. Hybrid FucoPol membranes were successfully applied in ethanol dehydration, with higher selectivity values than

commercial membranes PERVAP® 4101. However, they lost their stability in contact with solutions of 10.0 wt.% water in ethanol after three days of operation. In contrast, when these membranes were applied for N_2 dehydration, they were stable, showed reproducible results and extremely high water selectivities.

Permeation of water vapour and pure gases (CO_2, CH_4 and N_2), at different conditions of gas humidity content was monitored by mass spectrometry. Gas mixtures containing 20 vol.% CO_2 + 80 vol.% N_2 and 70 vol.% CH_4 + 30 vol.% CO_2 were also studied to mimic industrial applications, namely flue gas and biogas dehydration. The hybrid membranes developed showed barrier properties to all gases studied, with a gas permeability below 1 barrer. On the other hand, they exhibited high water permeabilities and selectivities. When processing the biogas mixture, the water permeability was found to be three times higher than water permeability in the flue gas mixture, leading to a H_2O/CH_4 selectivity much higher than H_2O/N_2 selectivity (4042 and 294, respectively). The hybrid FucoPol membranes showed that, in real situations, have the capacity to dehydrate mixtures, with the advantage of not losing N_2 or CH_4, due to the low permeability values of these gases.

This work shows that microbial polysaccharides obtained from a renewable source and purified without using solvents can be a sustainable alternative to other materials used in industrial dehydration processes. Strategies for further improvement should include optimization of polymer cross-linking conditions and optimization of the thickness of the active layer of the composite membranes in order to improve the long term stability of the membranes and promote higher fluxes, without compromising selectivity.

Keywords: Microbial polysaccharides, Membrane development; Membrane characterisation, Sol-gel method, Ethanol dehydration, Gas dehydration.

RESUMO

Este trabalho de doutoramento propõe o uso de dois exopolissacarídeos microbianos, GalactoPol e FucoPol, para o desenvolvimento de membranas de modo a serem aplicadas em processos de desidratação relevantes na indústria. O material de partida é obtido a partir de uma fonte de carbono abundante e de baixo custo, o glicerol produzido como subproduto da indústria de biodiesel, o que representa uma vantagem económica importante.

Foi dada uma atenção especial ao desenvolvimento de membranas com melhores propriedades mecânicas e de transporte, e elevada seletividade à água para aplicação em processos de desidratação por pervaporação e permeação de vapor. As abordagens selecionadas para o melhoramento das propriedades das membranas incluíram a reticulação do polímero e o desenvolvimento de membranas híbridas usando o método sol-gel.

Em primeiro lugar, as membranas foram modificadas usando diferentes agentes de reticulação: ácido tricloroacético para GalactoPol e "genipin" para Fucopol. Foram estudados diferentes protocolos de reticulação para avaliar o seu potencial na desidratação de etanol por pervaporação. Estas membranas foram caracterizadas em termos da sua estrutura morfológica, resistência a solventes e propriedades mecânicas. As membranas mostraram elevada afinidade para a água, boa resistência química em relação a solventes orgânicos e propriedades mecânicas adequadas. As experiências de pervaporação foram realizadas utilizando ambos os tipos de membranas para diferentes concentrações de água na corrente de alimentação (5,0 a 10,0 wt.%) a uma temperatura constante de 30ºC.

Além disso, também foi estudado qual o impacto do método de purificação dos exopolissacarídeos - por diálise e por dia-ultrafiltração - nas propriedades e no desempenho de transporte das membranas compósitas de FucoPol para pervaporação. Encontraram-se diferenças significativas na estrutura das membranas, na presença de água, e na seletividade, dependendo do método de purificação. A tensão de corte imposta durante a purificação pelo método de dia-ultrafiltração conduziu a uma desintegração dos agregados de polissacarídeos e, como consequência, obtiveram-se membranas mais densas, que afectaram o seu desempenho de transporte. As membranas desenvolvidas, em particular, a membrana compósita de GalactoPol-PES e a membrana obtida por dia-ultrafiltração FucoPol-PES, exibiram grande potencial de desidratação do etanol, uma vez que se alcançou uma seletividade de água / etanol de 134 e 143, respectivamente, em soluções de 10,0 wt.% de água em etanol.

Embora, as membranas desenvolvidas tenham uma excelente afinidade para a água tornam-se progressivamente instáveis em soluções aquosas. Assim, membranas híbridas de FucoPol foram desenvolvidas de modo a combinar as melhores propriedades da rede inorgânica com a seletividade dos polissacarídeos microbianos, a serem aplicados em processos de pervaporação para desidratação de etanol, bem como em desidratação de gases. As membranas híbridas foram preparadas por incorporação de uma rede de SiO_2 homogeneamente dispersa pelo

método de sol-gel usando (3-Glycidyloxypropyl) trimethoxysilane (GPTMS) como precursor de sílica de reticulação. Estas membranas foram caracterizadas estruturalmente, mecanicamente e termicamente. Apresentaram uma estrutura densa e homogênea, resistente à deformação, uma temperatura de transição vítrea (Tg) de 43ºC e uma decomposição térmica entre 240-251ºC. As membranas híbridas de FucoPol foram aplicadas com sucesso em desidratação de etanol, com valores de seletividade mais elevados do que as membranas comerciais PERVAP® 4101. Contudo, perderam a sua estabilidade em contato com soluções de 10,0 wt.% de água em etanol após três dias de operação. Em contraste, quando estas membranas foram aplicadas para a desidratação de N_2, elas apresentaram-se estáveis, com resultados reprodutíveis e seletividades de água extremamente elevadas.

A permeação de vapor de água e gases puros (CO_2, CH_4 e N_2), em diferentes condições de humidade, foi monitorizada por espectrometria de massa. Foram também estudadas misturas de gases contendo 20 vol.% de CO_2 + 80 vol.% de N_2 e 70 vol.% de CH_4 + 30 vol.% de CO_2 de modo a simular aplicações industriais, nomeadamente desidratação de gases de combustão e de biogás, respectivamente. As membranas híbridas desenvolvidas apresentaram propriedades de barreira para todos os gases estudados, com permeabilidades inferiores a 1 barrer. Por outro lado, exibiram elevadas permeabilidades e seletividades à água. Ao processar a mistura de biogás, verificou-se que a permeabilidade à água era três vezes superior à permeabilidade à água na mistura de gases de combustão, levando a uma seletividade de H_2O/CH_4 muito maior que a seletividade de H_2O/N_2 (4042 e 294, respectivamente). As membranas híbridas de FucoPol mostraram ter em situações reais a capacidade de desidratar misturas, com a vantagem de não perderem N_2 ou CH_4, devido aos baixos valores de permeabilidade desses gases.

Este trabalho mostra que os polissacarídeos microbianos obtidos a partir de uma fonte renovável e purificados sem o uso de solventes podem ser uma alternativa sustentável a outros materiais utilizados nos processos industriais de desidratação. Estratégias para melhorias adicionais devem incluir optimização das condições de reticulação do polímero e optimização da espessura da camada ativa das membranas compósitas, a fim de melhorar a estabilidade a longo prazo.

Palavras-chave: Polissacarídeos microbianos, Desenvolvimento de membranas, Caracterização de membranas, Método de sol-gel, Desidratação de etanol, Desidratação de gases.

CONTENTS

1 Introduction: motivation and objectives 1

1.1 Objectives 3

1.2 Thesis outline 3

2 State of the Art 7

2.1 General context 7

2.2 Hydrophilic pervaporation 8

2.3 Vapour permeation 10

2.4 Membranes 11

2.5 Biopolymers 14

2.5.1 Biopolymers in ethanol dehydration by pervaporation 15

2.5.2 Biopolymers in gas dehydration by vapour permeation 18

3 A New Microbial Polysaccharide Membrane for Ethanol Dehydration by Pervaporation 21

3.1 Summary 21

3.2 Introduction 22

3.3 Experimental 23

3.3.1 Materials 23

3.3.2 Membrane preparation 24

3.3.3 Membrane characterisation 24

3.3.4 Sorption experiments 26

3.3.5 Pervaporation experiments 26

3.3.6 Analytical methods 27

3.4 Results and discussion 27

3.4.1 Membrane characterisation 27

3.5 Conclusions 39

4 Impact of Biopolymer Purification on the Structural Characteristics and Transport Performance of Composite Polysaccharide Membranes for Pervaporation 41

4.1 Summary 41

4.2 Introduction 42

4.3 Material and methods 43
4.3.1 Materials 43
4.3.2 Methods 43
4.3.3 Characterisation of the active layer of the composite membranes 45
4.3.4 Mechanical properties 46
4.3.5 Pervaporation experiments 46
4.3.6 Polysaccharide solutions characterisation 46
4.3.7 Rheological characterisation 47
4.3.8 Polysaccharide particle size characterisation 48
4.4 Results and discussion 49
4.4.2 Structural and mechanical analysis of composite membranes 52
4.5 Pervaporation experiments 54
4.6 Polysaccharide solutions characterisation 57
4.6.1 Impact of purification methods on the chemical composition of polysaccharide solutions 57
4.6.2 Rheological characterisation of the membrane forming solutions 59
4.6.3 Polysaccharide particle size characterisation 61
4.7 Conclusions 63
5 Development and Characterisation of Hybrid Polysaccharide Membranes for Dehydration Processes 65
5.1 Summary 65
5.2 Introduction 66
5.3 Experimental 67
5.3.1 Materials 67
5.3.2 Membrane preparation 68
5.3.3 Characterisation of the hybrid polysaccharide membranes 69
5.3.4 Transport performance and stability of the hybrid membranes for ethanol dehydration 72
5.3.5 Transport performance and stability of the membranes for gas dehydration 73
5.4 Results and discussion 73
5.4.1 Selection of hybrid membrane composition 73

5.4.2 Characterisation of the hybrid polysaccharide membranes 74
5.4.3 Transport performance and stability of the hybrid membranes for ethanol dehydration by pervaporation 81
5.4.4 Transport performance and stability of the membranes for gas dehydration 84
5.5 Conclusions 85
6 Evaluation of Hybrid Polysaccharide Membranes for Gas Dehydration using On-line Mass Spectrometry 87
6.1 Summary 87
6.2 Introduction 87
6.3 Experimental 89
6.3.1 Materials 89
6.3.2 Membrane preparation 89
6.3.3 Single and mixed gas permeation experiments under dry and humidified conditions 90
6.3.4 Calibration method 92
6.3.5 Calculation methods 92
6.4 Results and discussion 93
6.4.1 Permeability for pure gases under dry conditions 93
6.4.2 Permeability for humidified gases – effect of water vapour on the permeability of pure gases 94
6.4.3 Permeability for gas mixtures – Flue gas and biogas dehydration 98
6.4.4 Membrane Stability 100
6.5 Conclusions 101
7 General Conclusions and Future Work 103
7.1 Suggestions for future work 105
Bibliography 107

LIST OF FIGURES

Fig. 3.1: Pervaporation (PV) experimental set-up: 1 – closed stirred feed vessel; 2 – recirculation pump; 3 – flat circular pervaporation module; 4 – pressure transducer; 5 – temperature sensor; 6 – condenser with liquid nitrogen; and 7 – vacuum pump. 26

Fig. 3.2: SEM views: (a) cross-section image of an EPS homogeneous membrane; and (b) cross-section image of a EPS-PES composite membrane. 28

Fig. 3.3: Representative stress-elongation curves and Young's modulus (slope of linear equations inside boxes) of the various materials exposed to air with 44.3% relative humidity at 22 ºC and immersed in 10.0 wt.% water in ethanol solution: (a) EPS membrane; (b) PES support; and (c) EPS-PES composite membrane. 31

Fig. 4.1: Scheme of the four purification methods used in rheological characterisation. 48

Fig. 4.2: Cross-section images obtained by SEM of the composite membranes prepared from polysaccharide purified by: (a) dialysis and (b) dia-ultrafiltration (magnification of 350 x)..... 53

Fig. 4.3: Determination of monosaccharide composition of the polysaccharides obtained by the two purification methods (dialysis and dia-ultrafiltration)..... 58

Fig. 4.4: Flow curves of the membrane forming solutions using the polysaccharide obtained with four different purification methods: dia-ultrafiltration; passage of the cell free fermentation broth through the pump and hollow fiber membrane module followed by dialysis (dialysis M); dialysis after a previous pump recirculation of the cell free fermentation broth (dialysis R); dialysis. 60

Fig. 4.5: Mechanical spectrum of the membrane forming solutions obtained from four purification methods: dia-ultrafiltration; passage of the cell free fermentation broth through the pump and hollow fiber membrane module followed by dialysis (dialysis M); dialysis after a previous pump recirculation of the cell free fermentation broth (dialysis R); dialysis. 61

Fig. 4.6: Z-average of polysaccharide aggregates in each step of membrane preparation with the polysaccharide solutions from dialysis and dia-ultrafiltration method. Step 1 – polysaccharide dissolved in distilled water; Step 2 – addition of Genipin; Step 3 – pH change; and Step 4 – temperature increase to 30 ºC. 62

Fig. 5.1: Schematic diagram of pervaporation system. FV: feed vessel; RP: recirculation pump (Lead Fluid BT/101S, China); PVM: pervaporation module; VP: vacuum pump (PFEIFFER Duo 2.5; Germany); C: condenser; V: valve; P: pressure transducer; T: temperature controller. 72

Fig. 5.2: i) FT-IR spectra of: a) pristine FucoPol; b) FucoPol+GPTMS 7 hybrid membrane and c) FucoPol+GPTMS 7+$CaCl_2$ hybrid membrane; ii) amplification of part of spectra of a) pristine FucoPol and b) FucoPol+GPTMS 7 hybrid membrane..... 74

Fig. 5.3: Thermograms of TGA analysis of FucoPol and hybrid polysaccharide membranes (FucoPol+GPTMS 7 and FucoPol+GPTMS 7+$CaCl_2$). 77

Fig. 5.4: DSC results for the FucoPol and hybrid polysaccharide membranes, with and without calcium chloride crosslinking - FucoPol+GPTMS7+$CaCl_2$ and FucoPol+GPTMS 7, respectively. 77

Fig. 5.5: SEM images of the hybrid polysaccharide membrane: a) surface and b) cross-section. 78

Fig. 5.6: Weight loss of the hybrid polysaccharide membranes (FucoPol) and LDPE film as a function of incubation time in soil. 81

Fig. 6.1: Experimental set-up for pure dry gas permeation. 90

Fig. 6.2: Experimental set-up for permeation in test mode (position 1) of: a) humidified single gas and b) humidified mixture of gases. 91

Fig. 6.3: Permeation experiment with dry CO_2: concentration of CO_2 in the permeate when using the FucoPol+GPTMS+$CaCl_2$ membrane, and corresponding permeability, represented against time (T=21 ºC and p_{perm}=70 mbar)..... 93

Fig. 6.4: Results for pure gas permeation with different gas humidity content. Note: the error bars in each measurement are, in some cases, smaller than the symbols. 94

Fig. 6.5: Water permeability for the humidified gases (CO_2, N_2 and CH_4) of the hybrid polysaccharide membrane at 22.0 ºC. Note: the error bars are smaller than the symbols. 95

Fig. 6.6: H_2O/gas (CO_2, N_2 and CH_4) selectivity for the dehydration process with the membrane FucoPol+GPTMS 7+$CaCl_2$ at 22.0 ºC. (GHC stands for gas humidity content wt.%). 96

LIST OF TABLES

Table 2.1: Pervaporation of ethanol solutions with 10 wt.% of water in the feed using membranes obtained from biopolymers. 17

Table 3.1: Swelling results of the homogeneous membrane of EPS at 23 ± 1 ºC. 29

Table 3.2: Average values obtained for the mechanical properties of the membranes developed and for the PES supporting material, for the two experimental conditions studied: exposure to air with 44.3% relative humidity at 22 ºC and immersion in 10.0 wt.% water in ethanol solution. ... 32

Table 3.3: Comparison of the mechanical properties of dense membranes composed by biopolymers. 33

Table 3.4: Mass fluxes of water and ethanol for the homogeneous membrane of EPS and for the composite membrane of EPS-PES. 34

Table 3.5: Values of calculated saturation vapor pressure at 30ºC (a) and activity coefficients (b) for water and ethanol. 35

Table 3.6: Comparison of permeability and selectivity values of water and ethanol for the homogeneous membrane of EPS and for the composite membrane of EPS-PES (a) and for other membranes referred in literature (b). 35

Table 3.7: Sorption coefficients for water and for ethanol, for the homogeneous membrane of EPS and for the active layer of the composite EPS-PES membrane. 37

Table 3.8: Ratio between water and ethanol permeabilities and ratio between water and ethanol sorption coefficients, calculated in a molar basis, for both membranes. 38

Table 4.1: Chemical analysis of the homogeneous membranes using polysaccharides purified by dialysis or by dia-ultrafiltration in two different conditions: (A) exposed at atmospheric conditions and (B) after immersion in a solution of 10.0 wt.% of water in ethanol. 50

Table 4.2: Swelling and leaching degree of the homogeneous membranes prepared using the polysaccharides obtained by dialysis or by dia-ultrafiltration. 51

Table 4.3: Results of mechanical properties (tensile tests) for both types of composite membranes (d/EPS-PES and DU/EPS-PES) in two experimental conditions: atmospheric conditions with a relative humidity (RH) of 48.0% and after immersion for 24 h in a solution of 10.0 wt.% water in ethanol. 54

Table 4.4: Mass fluxes (total, water and ethanol) of both composite membranes (T=30 ºC; downstream pressure = 1.5 ± 0.1 mbar). 55

Table 4.5: Water and ethanol permeability and selectivity values for composite membranes of polysaccharide obtained by the two purification methods: dialysis and dia-ultrafiltration, referred as d/EPS-PES and DU/EPS-PES, respectively. 56

Table 4.6: Comparison of the transport properties of the DU/EPS-PES composite membrane with other membranes referred in the literature. 56

Table 4.7. Ion content in the polysaccharide solutions purified by dialysis and by dia-ultrafiltration determined by ICP-AES. 58

Table 5.1: Hybrid polysaccharide membranes prepared using different concentrations of GPTMS SiO_2 precursor in the sol-gel method. 69

Table 5.2: TGA results of FucoPol and the hybrid polysaccharide membranes prepared. 76

Table 5.3: Swelling and leaching of the FucoPol+GPTMS 7+$CaCl_2$ membranes. 79

Table 5.4: Mechanical properties of the hybrid polysaccharide membrane before crosslinking with $CaCl_2$ (FucoPol+GPTMS 7) and after crosslinking (FucoPol+GPTMS 7+$CaCl_2$). 79

Table 5.5: Transport performance of FucoPol+GPTMS 7+$CaCl_2$ developed by the sol-gel process (T=30.0 ºC; downstream pressure = 1.0 mbar). 82

Table 5.6: Comparison of the transport performance of FucoPol+GPTMS 7+$CaCl_2$ with other membranes, referred in literature for ethanol dehydration. 83

Table 5.7: Stability of the hybrid polysaccharide membrane in three pervaporation consecutive experiments (using wet membranes in a solution of 10 wt.% of ethanol in water, with an interval of 24 h). T=30 ºC and downstream pressure 1.0 mbar. 84

Table 5.8: Results of nitrogen dehydration by vapour permeation over time (absolute downstream pressure of ~70mbar, RH=52%, and $t_{experiment}$=6h each during three consecutive experiments). 85

Table 6.1: Permeability for dry gases. 93

Table 6.2: Comparison of transport performance of different membranes referred in the literature. GHC corresponds to gas humidity content. 97

Table 6.3: Transport performance of the hybrid polysaccharide membrane for synthetic flue gas and biogas dehydration. 99

LIST OF ACRONYMS

Abbreviations

3D – three-dimensional

Alg – sodium alginate

AlgCa+Fe_3O_4 – alginate crosslinked with ions of Ca^{2+} and incorporated with ferroferric oxides

BC – bacterial cellulose

BFC – back pressure controller

C - condenser

CER – cationic exchange resin

CDA – cellulose diacetate

CLM – contained liquid membranes

CMC - carboxymethylcellulose

CS – chitosan

CS-Ti-DHPPA/PAN – chitosan incorporated with a $TiCl_4$ using as modifier 3-(3,4-Dihydroxyphenyl)propionic acid (DHPPA), and polyacrylonitrile as support of composite membrane

d/EPS-PES – composite membrane with an active layer of polysaccharide purified by dialysis

DLS – dynamic light scattering

DNA-Na – deoxyribonucleic acid sodium salt

DO – dissolved oxygen

DSC – differential scanning calorimetry

DU/EPS-PES – composite membrane with an active layer of polysaccharide purified by dia-ultrafiltration

EDX – energy dispersive X-ray spectroscopy

EPS – exopolysaccharide or extracellular polysaccharide

FID – flame ionization detector

FT-IR – fourier transform infrared spectrometry

FV – feed vessel

G – gas to be studied

GA – glutaraldehyde

GC – gas chromatography

GHC – gas humidity content

GPTMS – (3-Glycidyloxypropyl) trimethoxysilane

HA – hyaluronic acid

HGS – humidified gas system

HPLC – high-performance liquid chromatography

ICP-AES – inductively coupled plasma atomic emission

ILM – immobilized liquid membranes

LDPE – low density polyethylene

LPG – liquefied petroleum gas

M – manometer

MC – membrane cell

ME – mixing element

MFC – mass flow controller

MOFs – metal organic frameworks

MS – mass spectrometry or mass spectrometer

MWCO – molecular weight cut-off

NaAlg – sodium alginate

P – pressure transducer

PAAHCl – poly(allylamine hydrochloride)

PALS – positron annihilation lifetime spectrometry

PAN – polyacrylonitrile

PEBAX® - polyether block amide

PEO-ran-PPO – poly(ethylene oxide) based block copolymers

PERVAP® – commercial membrane of poly(vinyl alcohol) from Sulzer Chemtech

PES – polyethersulfone

PFSI – perfluorosulphonic acid ionomeric membrane

PHA – polyhydroxyalkanoates

PLA – polylactic acid

PS – polysulfone

PSf/Si-TFN – nanocomposite polysulfone with nanosilicon particles

PSI – pervaporation separation index

PV – pervaporation

PVA – poly(vinyl alcohol)

PVDF – polyvinylidene fluoride

PVM – pervaporation module

RF – radio-frequency

RH – relative humidity

RP – recirculation pump

SEM – scanning electron microscopy

SLM –supported liquid membrane

SPEEK – sulfonated polyetheretherketone

T – temperature controller

TCA – trichloroacetic acid

TEOS - tetraethylorthosilicate

TFA – trifluoroacetic acid

TGA – thermogravimetry analysis

TH – thermohygrometer

THF – tetrahydrofuran

TMP – transmembrane pressure

TR-HAB-6FDA-PBO – polyimide blend films

V – valve

vol - volumetric fraction

VP – vacuum pump

wt – weight fraction

Variables

A – membrane area (m^2)

D – diffusion coefficient (m^2/s)

f – frequency (Hz)

G' – storage moduli (Pa)

G'' – loss moduli (Pa)

J – molar flux ($mol/m^2.s$)

J_t – total flux ($g/m^2.h$) or ($kg/m^2.h$)

l – thickness (m)

m – mass (g) or (kg)

m_1 – weight of membrane at room humidity and temperature (g)

m_2 – weight of swollen membrane (g)

m_3 – weight of dry membrane (g)

m_{H2O} – weight of water in membrane (g)

m_{SiO2} – mass of silica (g)

M_{SiO2} – molecular weight of silica (g/mol)

n_{GPTMS} – number of moles of GPTMS (mol)

p – partial pressure (Pa)

P – permeability (mol/m.s.Pa) or (barrer)

p^{sat} – saturation vapour pressure (Pa)

Q_{Ar} – volumetric flowrate of standard gas argon (m^3 [STP] / s)

S – sorption coefficient (-)

t – time (s) or (h)

T – temperature (ºC)

Td – temperature of degradation (ºC)

Tg – glass temperature (ºC)

x – molar fraction of the compounds in the permeate (-)

x_{SiO2} – weight fraction of silica (-)

Wd – weight of the membranes dried after swelling experiments (g)

Wf – weight of swollen membrane (g)

Wi – weight of dry membrane (g)

y – molar fraction of the components in the feed (-)

Greek symbols

α – selectivity (-)

Ύ – activity coefficient (-)

δ – thickness (m)

Subscripts

et – ethanol

feed – feed side

i – compound i

perm – permeate side

pure – pure liquid compounds

sat – saturation

w – water

wet – wet membrane

Chapter 1

1 INTRODUCTION: MOTIVATION AND OBJECTIVES

Solvent dehydration processes have a high economic and environmental relevance in industry. Organic solvents are commonly used in pharmaceutical and chemical industry in several applications, such as, synthesis of pharmaceuticals, solvent extraction and drying of final products. However, most solvents used contain a certain amount of water and have to be purified and recycled, being dehydration an essential step in their recovery.

The most important solvents to be treated are light alcohols (ethanol, isopropanol and butanol), esters (ethyl and butyl acetate), ketones (butanone and methyl ethyl ketone), ethers (tetrahydrofuran and acetonitrile) or mixtures of these solvents, which may form azeotropes with water.

Among all liquid separation techniques, distillation is the most widely applied technique. However, distillation consumes large amounts of energy and it is limited when dealing with azeotropic mixtures or close-boiling point mixtures. For such systems, a higher purity product cannot be achieved using conventional distillation, being necessary to develop alternative methods to satisfy these requirements.

Pervaporation is a promising process for separating azeotropic mixtures, close-boiling mixtures, and for the dehydration of solvents. Moreover, pervaporation is attractive due to its relative simplicity of operation and high selectivity, which translates into a process economy. Suitable membranes yielding high permeability, good selectivity and sufficient mechanical strength are needed, because they impact on the cost of the installation, the plant performance and the membrane lifetime.

At present, there is a growth of emissions of undesired gases from industries into the atmosphere that cause environmental pollution and climate change, creating a global warming problem. Thus, it is mandatory to reduce gas emission to the atmosphere and use energy from renewable resources. In particular, CO_2 separation and capture from coal- or natural gas- fired power plants is recognized as an important step to deal with a global warming and rapidly increasing energy consumption, since they are major contributors to the greenhouse effect. The burning of coal, for example, will produce tremendous amounts of flue gas (composed essentially by nitrogen, water vapour and carbon dioxide), which is the main reason for the hazy weather. Thus, gas(es) purification or gas cleaning of power plants before emission into the atmosphere is essential for removing the pollutants present.

On the other hand, the use of energy from renewable resources, as an alternative to fossil fuels, such as biogas, can be mandatory to create a sustainable environment. The biogas is a cleaner and versatile fuel, which can be enriched and purified to produce natural gas.

Among the impurities available, water vapour is the most common, being gas dehydration a relevant industrial issue. When water is present in gas streams many problems may occur: (1) water can freeze and/or form solid hydrates, reducing the gas flow or plugging the line; (2) water collected in pipelines can increase the pressure drop and/or cause slug flow; and (3) when acid gases (H_2S and CO_2) are dissolved in free water can cause severe corrosion and erosion in pipes and process equipment.

Conventional methods for gas dehydration, such as absorption/adsorption by liquid/solid desiccants, involve high energy consumption and large size equipment, hence, the application of membrane technology in gas separation and dehydration, is promising and attractive in order to save energy and allowing possible re-use of water, combine inherent simplicity and small footprint.

When compared with solvent absorption techniques, membrane-based gas capture technologies can be technically, energetically and economically advantageous. However, most studies reported in literature, consider only membrane separation in the presence of dry pure gases. Separation of gases (namely CO_2) in the presence of minor components like hydrogen sulphide (H_2S) and water vapour is still rarely addressed. Water vapour removal is particularly important and can be applied in vast areas in industry, such as gas dehydration (flue gas, biogas and natural gas), drying of compressed air, steam recovery and air treatment for packaging and processing industries.

Membranes are the heart of pervaporation and gas dehydration membrane processes. Polymeric membranes dominate the membrane separation industry, due to their diversity, scalability, economic competiveness and simple fabrication methods. A particular attention is given to the development of new membranes with enhanced mechanical and transport properties, and enhanced water selectivity for application in solvent dehydration by pervaporation and gas dehydration. Among the available materials, biopolymers, in particular natural polysaccharides, have received much attention due to their solvent resistance, high affinity for water and high separation performance. Microbial polysaccharides represent better alternatives to the referred materials, since microorganisms are generally better suited for polysaccharide production than plant or algae, exhibiting higher growth rates. However, the high cost of carbon sources used, mainly glucose, sucrose and fructose limits the potential market of these biopolymers.

Recently, it has been reported that by-product streams containing glycerol, from biodiesel production, could be applied as carbon source to produce two extracellular polysaccharides (EPS), with attractive productivity and polymer yield. These new EPS are high molecular weight negatively charged heteropolysaccharides, composed by sugars (galactose, glucose, fucose, mannose and rhamnose) and acyl groups (pyruvil, succynil and acetyl). The GalactoPol produced

by *Pseudomonas oleovorans* is composed by 68% galactose, 13% glucose, 17% mannose and 2% rhamnose, as well as, 3% of acyl groups [1]. While the FucoPol is produced by *Enterobacter* strain A47 and is composed by fucose (37-42%), galactose (18-23%), glucose (28-34%) and glucoronic acid (6-12%) [2].

This thesis proposes the development of membranes based on these new exopolysaccharides to be applied in relevant dehydration processes for industry, namely ethanol dehydration by pervaporation and dehydration of gases, such as flue gas and biogas.

1.1 Objectives

The main objectives of this PhD work are:

I. Development of new membranes based on microbial extracellular polysaccharides (EPS), produced from glycerol of by-product streams of biodiesel factories. Membranes with enhanced water resistance and water selectivity need to be developed using selected strategies.

II. Characterisation of the membranes developed in terms of thermal and mechanical properties, internal and surface morphology, resistance to selected solvents, transport properties (namely selectivity for water), life-time and biodegradability. The impact of biopolymer purification on the structure and transport properties of the membranes, will be also addressed.

III. Evaluation of the membranes developed in dehydration processes: solvent dehydration by pervaporation and gas dehumidification and application to selected systems with industrial relevance (ethanol dehydration, biogas and flue gas dehumidification).

1.2 Thesis outline

This thesis comprises six chapters. After Introduction, each chapter is organized in summary, introduction, materials and methods, results and discussion, and conclusions. The methodologies used in each chapter are described in detail within the context of the respective subject. On the other hand, it is important to note that in each chapter the exopolysaccharide used was obtained from a different batch production. The last chapter reports the main conclusions and suggestion for future work.

A summary of the content of each chapter is described below:

Chapter 1 – **Introduction** - describes the motivation for this PhD work and the objectives proposed.

Chapter 2 **– State of the art -** introduces the actual state of the art of the subject developed in this thesis. The content of this chapter was partially based on chapter 10: I.T. Meireles, C. Brazinha, I.M. Coelhoso, J.G. Crespo, "Membranes for ethanol dehydration" of the book entitled "Membrane Technologies for Biorefining", 1st Ed., 2016. Editors: Alberto Figoli, Alfredo Cassano & Angelo Basile, 241-263.

Chapter 3 – **A new microbial polysaccharide membrane for ethanol dehydration by pervaporation** - reports the characterisation and transport performance of this new exopolysaccharide (GalactoPol) extracted with acetone from the fermentation broth and crosslinked with a solution of trichloroacetic acid (TCA). In this study, two types of membranes were prepared: homogeneous (EPS) and a composite of EPS and polyethersulfone (EPS-PES), used as support. Both membranes were characterised and were used for ethanol dehydration by pervaporation for two different water concentrations in the feed phase (5.0 and 10.0 wt%), at a constant temperature of 30ºC. The content of this chapter was published in Journal of Membrane Science 425-426 (2013) 227-234.

Chapter 4 – **Impact of biopolymer purification on the structural characteristics and transport performance of composite polysaccharide membranes for pervaporation –** in this chapter the purification of the FucoPol from complex culture media was performed using two different processes: dialysis and dia-ultrafiltration. The membranes prepared using the biopolymer obtained by these two methods were compared in terms of structure, resistance to solvents, mechanical and transport properties for ethanol dehydration by pervaporation. The content of this chapter was published in Journal of Membrane Science 493 (2015) 179-187.

Chapter 5 - **Development and characterisation of hybrid polysaccharide membranes for dehydration processes –** presents the development and characterisation of hybrid polysaccharide membranes prepared by a sol-gel process and evaluates their performance in dehydration processes, by pervaporation and vapour permeation. The purpose of this study was to prepare and characterise novel hybrid polysaccharide membranes combining the best properties of the inorganic network with the selectivity of the polysaccharide material, in order to assess the potential of this membrane in ethanol and N_2 dehydration. The content of this chapter was submitted to Carbohydrate Polymers journal.

Chapter 6 – **Evaluation of hybrid polysaccharide membranes for gas dehydration using on-line mass spectrometry** – studies the application of the membranes developed in Chapter 5 in gas dehydration. This work studies the effect of the presence of water vapour on gas permeability and selectivity, using single gases and mixtures of gases, namely CH_4/CO_2 and N_2/CO_2. These studies are required in order to assess the use of these membranes in relevant industrial dehydration processes, such as biogas and flue gas processing. The results of this chapter was submitted to Journal of Membrane Science.

Chapter 7 - **Conclusions and future work –** reviews the main results obtained in this PhD project and presents the main conclusions. Additionally, some suggestions and challenges for future work are also proposed.

Chapter 2

2 STATE OF THE ART

This chapter was partially adapted from: Inês T. Meireles, Carla Brazinha, Isabel M. Coelhoso, João G. Crespo, Membranes for ethanol dehydration, of the book entitled "Membrane Technologies for Biorefining", 1st Ed., 2016. Editors: Alberto Figoli, Alfredo Cassano & Angelo Basile, 241-263.

2.1 General context

The global economy is completely dependent on energy, a key factor for industrial development and human life. The most common industrial separation processes, such as distillation, evaporation and freeze-crystallization, are energy-intensive methods [3]. Consequently, the improvement of the current separation processes is mandatory.

Membrane based technologies may offer advantages over traditional separations methods, since they use compact and modular systems with high selectivity and low energy consumption. Moreover, they may reduce product degradation, allowing for designing novel process solutions being generally regarded as environmentally friendly. They can be applied in several types of processes, such as purification, concentration and fractionation; also, they allow for creating hybrid separation concepts combining membranes and other separation processes [3–6].

In the last years, membrane technologies have been used in a wide range of applications, such as sea water desalination, concentration and purification of food and pharmaceutical products, fuel cells and drug delivery devices [7]. Other applications also emerged, as liquid mixtures separation by pervaporation and vapour and gases purification.

Liquid separations are very important in many industries, but among all separation techniques available, thermal separation processes, like distillation, are still the most used processes. Distillation consumes more than 95% of total the energy spent for separation process in the chemical industry, although it is limited in the separation of complex mixtures, such as azeotropic mixtures and close boiling point mixtures, where the use of entrainers is needed to recover pure solvents [6,8].

Compared to traditional separation techniques, pervaporation is preferred since this membrane process requires a moderate energy input and, if the right conditions are used, may be more selective than non-membrane processes [9,10]. The major advantage of pervaporation is its high solute selectivity, when compared to conventional evaporative processes, such as distillation and membrane distillation. Pervaporation is not regulated by liquid-vapour equilibrium thermodynamics because, in fact, this process involves a sorption-diffusion-desorption

mechanism. For this reason, azeotropes are not formed and, if the membrane is correctly designed, much higher solute/solvent selectivities may be obtained, although at expenses of lower fluxes. As pervaporation membranes are selected to have higher affinity to the solute than to the solvent, leading to a high sorption selectivity, the ratio of the permeabilities is always higher than 1. Moreover, pervaporation does not require any additional extracting agent / entrainer and is particularly appropriate to recover highly diluted solutes from processing streams as the separation process is based on distinct molecular interactions between the membrane and the solute or the solvent with an aimed selective solute sorption.

On the other hand, distillation is also limited for dehydration of organic solvents when they form azeotropic mixtures with water. A classic example of this kind of mixtures, is the ethanol-water system, which forms an azeotrope around 4.4 wt.% of water [11,12]. To dehydrate organic solvents, hydrophilic pervaporation offers potential solutions and competes directly with traditional processes like distillation, liquid-liquid extraction, adsorption and stripping [13].

Other application where membrane technology has been expanding rapidly is vapour permeation. In this process the use of membranes reduces energy and other operational cost [14,15].

Membrane-based dehydration (or drying) of gas streams has several advantages when compared to other dehumidification methods. Using membrane technology, the water is removed from the gas stream without phase transition [16], which makes the process more energy efficient. This technology uses hydrophilic polymers, since the groups present in this type of polymers are able to interact with water molecules, and thanks to this, water is adsorbed and diffuses through the polymers [17,18]. Applications such as dehydration of natural gas and flue gas, compressed air drying, ventilation latent-heat recycling, among others can benefit from the use of membrane-based dehydration [19].

Membranes, as the functional layer for separation, are the main component of pervaporation and gas dehydration processes. The membrane material determines the permeation and selectivity and hence the separation properties of the process [14,18]. Consequently, researchers from both industry and academia have dedicated great attention to the design of membranes with appropriate chemistry, morphology and separation performance [14].

2.2 Hydrophilic pervaporation

Contrary to organophilic pervaporation and pervaporation of organic mixtures, hydrophilic pervaporation is an established industrial process, with the dehydration of ethanol and isopropanol, respectively as the 1st and 2nd main applications [19,20]. The success of hydrophilic pervaporation is explained by the advantages of pervaporation in general, mentioned in section 2.1. and, as a consequence of that, hydrophilic pervaporation has no restrictions in processing azeotropic mixtures, avoiding the constraints imposed by liquid-vapour equilibrium to the traditional distillation processes. Furthermore, as water is a small molecule with a high diffusivity

in the membrane, hydrophilic pervaporation tends to be more selective than organophilic pervaporation and pervaporation of organic mixtures, due to its high diffusivity selectivity (in relation to the solvent ethanol, a larger molecule). As water has also high water diffusivity in the feed solution adjacent to the membrane, the mass transport resistance that may be built adjacent to the membrane, with a consequent building of a feed boundary layer, tends to be less important in hydrophilic pervaporation than in organophilic pervaporation and pervaporation of organic mixtures.

Comparing with distillation technology, pervaporation has been identified as one of the most efficient separation processes for dehydration of bioalcohols, with energy savings up to 50% [21]. Additionally, hydrophilic pervaporation was compared to azeotropic distillation for the dehydration of 94.9 wt.% to 99.8 wt.% of ethanol in a full-scale plant at 70 °C at a rate of 150 kL/day. Pervaporation was estimated to cost $21–26/ton, approximately 1/3–1/4 of that for azeotropic distillation [22]. A similar result was obtained by the company Lurgi when comparing the cost of ethanol dehydration from 94.0 wt.% to 99.8 wt.% of ethanol during a 12-month run of a Lurgi industrial pervaporation system. The cost of 62–89 and 22–30 Deutsch Mark per tonne of produced anhydrous ethanol (99.8 wt.% ethanol) were obtained respectively when using azeotropic distillation (with cyclohexane as entrainer) and pervaporation [23]. When comparing molecular sieve adsorption (another current technology for bioethanol dehydration) to hydrophilic pervaporation, a pervaporation unit with 120 m^2 of membrane area may be replaced by a 160 ton molecular sieve adsorption unit for an annual production of 200,000 ton of ethanol at a concentration higher than 99.5%. Unlike the molecular sieve adsorption, hydrophilic pervaporation uses no steam and requires a lower energy consumption [10].

The interest on hydrophilic pervaporation for ethanol dehydration has started in 1980’s, but was more extensively studied from the 1990’s. Since 2008-2010, research on hydrophilic pervaporation has been focusing on the ability to develop highly performing membranes, aiming high selectivities and productivities (fluxes), able to operate in a stable mode under specific environmental conditions. In this sense, special attention has been given to the development of new materials, stable and with an extended lifetime.

The first commercial application of pervaporation was, in fact, the dehydration of ethanol. In 1983, Tusel and Ballweg [24] patented a system combining a distillation column followed by two pervaporation units. After this, membrane technologies have been integrated into bioethanol production processes and companies such as PetroSep Membrane Research Inc. (Canada), Mitsui (Japan) and Sulzer Chemtech (Germany) began to commercialise membranes for pervaporation applications [25]. From 1990 to 2010, the market for pervaporation/vapor permeation equipment was about $20 million/year [26], with more than 100 plants for ethanol dehydration installed [27]. Despite the advantages above described, hydrophilic pervaporation still did not achieve to become the dominating technology, replacing azeotropic distillation and molecular sieve adsorption. Nevertheless, there are excellent opportunities for hydrophilic pervaporation with the prediction that between 300 and 500 of cellulose-to-ethanol plants will be

built by 2022 [26]. Hydrophilic pervaporation may be coupled to conventional distillation (for processing streams with dilute ethanol concentrations) and, eventually, coupled to molecular sieve adsorption (for processing streams with near 100%).

2.3 Vapour permeation

Vapour permeation, such as hydrophilic pervaporation, has been established as an improved technology [28]. Vapour permeation is a process where a saturated vapour contacts with the feed surface of the membrane as a semi-permeable barrier and a vacuum or a sweeping gas flow is used in the permeate side of the membrane. The permeated vapour is taken out by vacuum or a sweeping gas flow and the purified gas remains in the retentate [29]. This separation works according to a solution-diffusion model, since different components are, firstly, adsorbed in the membrane at the feed side; secondly, they diffuse through the membrane and at the downstream side of the membrane they desorb to the permeate [18,30]. The partial pressure difference of each component between the feed and permeate side is the driving force for mass transfer [18,29].

Although the membranes used in vapour permeation may be the same used in pervaporation, the first industrial installation has been developed only recently [3,31]. The first vapour permeation industrial process plant was built in Germany only in the end of 1980's for ethanol dehydration [31]. In the last years, more than 160 units of vapour-gas separation were installed in the world, but this number is clearly increasing, indicating the growing importance of vapour permeation processes in industry [32,33]. The main industrial application of vapour permeation is the recovery of hydrocarbon vapours from light gases (nitrogen, methane, hydrogen, etc.). However, other applications are highly relevant in industry, such as: the recovery and recycling of monomers such as ethylene, propylene and vinyl chloride, in the petrochemical industry; the recovery of liquefied petroleum gas (LPG) in remote areas; and, in natural gas industry, namely for removing acid gases, CO_2 and water vapour [32].

The transport of water vapour, in particular, is attracting a high interest from researchers, since water can interact with the polymer chains, inducing swelling and plasticization of the membranes, and ultimately leading to ageing effects [34,35]. Moreover, in many industrial processes the recovery of water vapour represents an additional energy saving, prevents corrosion problems and can alleviate haze pollution [36,37]. Therefore, dehydration of gases has a major industrial importance, since this process can be used for the dehydration of natural gas, drying of compressed air, packaging materials, roofing covers, humidity control in closed spaces, such as air conditioning in buildings, aviation and space flight. Additionally, water can be recovery from waste steam, which may be of interest in many industrial process [18,38].

To remove water vapour from gas streams, several techniques can be used, such as: adsorption using a desiccant drying system, solvent absorption using, for example, diethylene or triethylene

glycol, condensation and membrane processes [16,36]. In the first process, the surface of a solid desiccant, like molecular sieves, captures the water vapour, while in the second process, the gas contacts with a solvent absorbent that has high affinity for water, but both need high temperatures (160-200 ºC) for regeneration and reuse of the ad/absorbents, and also generate low quality water. As a consequence, both processes involve consumption of high quantities of energy, are difficult to scale up and have high cost of maintenance [36,37,39,40]. In the case of condensation, the condensed water is dirty and corrosive, due to the simultaneous removal of impurities (such as foam and dust), and, therefore, cannot be reused. On the contrary, when using a membrane process, the selective removal of water vapour from gas streams produces water with high purity. Moreover, the membrane technology involves a low energy consumption (since the only energy cost is to maintain a partial pressure difference across the membrane [16]), small footprint, has a flexible and compact design, modulated and easy to maintain and control [41,42].

Although conventional processes, like absorption, hold the major part of the gas dehydration market, membrane separation processes are gaining a progressive attention. However, absorption processes still have a lower cost when compared with membrane vapour permeation using conventional commercial membranes [43]. New membrane materials, with extremely high water vapour permeability and selectivity over non-condensable gases are needed to meet the challenges, in order to make the process economically competitive [36,44].

2.4 Membranes

For removal of water from mixtures of water/organic liquid or vapour mixtures, the material used in the membrane depends on the components to be separated but, generally, hydrophilic materials are preferred because water is preferentially absorbed and diffuses through these materials [3,18]. In the last decades, various membranes have been tested in dehydration processes by pervaporation and vapour permeation. However, just a few of them satisfy the requirements necessary for industrial application. Namely, high permeance and selectivity combined with good chemical and mechanical stability at high temperatures, with a reasonable cost [45].

Membranes fall into two categories: homogeneous membranes and composite membranes [46]. Homogeneous membranes consist of a dense thick film, while composite membranes consist of one or more polymeric or ceramic layers, where the selective layer is coated over a porous substrate. In composite membranes, the selective layer controls the mass transport of species through the membrane and the support provides the mechanical stability for the selective layer [47]. Due to the much thinner thickness of the top layer of composite membranes, these can offer a higher permeation flux than homogeneous membranes [46]. However, the preparation of composite membranes, with a small thickness of selective layer, can be limited by the porosity, pore size and roughness of the membrane support [48]. Ideally, the support of a composite

membrane should present a negligible resistance to membrane transport, in order to not diminish the membrane flux and selectivity [46].

There are four main classes of membranes based on the nature of the membrane material: polymeric membranes (such as PVA, polysulfone (PS), chitosan, etc.), based on organic polymer chains that are crosslinked together; inorganic membranes, like ceramics or zeolites; mixed matrix membranes, comprising an organic polymer with inorganic particles dispersed throughout the polymeric matrix; and liquid membranes [8,15,49], which consist of a liquid phase retained inside the pores of a supporting porous material.

Polymeric membranes are widely used in dehydration processes, since they have innumerous advantages, such as compactness, ease of fabrication and scale-up and low cost per unit area [15,50]. The material and structure of the membrane determine its performance and, normally, these membranes are made of rigid chain polymers that are capable of ion-dipole interactions or hydrogen bonding with water, acting as molecular sieves, adsorbing preferentially water instead of other molecules [8].

Many researchers have developed efforts to improved membrane stability by crosslinking and blending, since the controlled crosslinking limits the mobility of the polymer chains, suppressing the swelling of the membrane. Alternatively, blending of the hydrophilic polymers with other polymers can increase the mechanical strength and stability of the membrane in aqueous solutions [51]. On the other hand, polymeric membranes have also other limitations, such as low thermal stability and chemical instability, which limits the performance of the process and the range of experimental conditions [15].

Inorganic membranes may offer significant advantages over polymeric membranes, due to higher solvent resistance and thermal stability. Inorganic membranes have no limitations in what concerns the range of permissible feed concentrations, due to the non-existence of membrane swelling effects [52]. Also, the ability of inorganic membranes (made from amorphous silica, carbon, zeolites, etc.) [15] to operate at high temperatures with high fluxes reduces the required membrane area for operation, comparatively to polymeric membranes [8]. However, inorganic membranes are more difficult to produce at large-scale and are significantly more expensive than polymeric membranes. Their harder structure can cause problems with brittleness in some cases [46] and their stability in acidic conditions is frequently inadequate [53]. Dense structures of inorganic membranes, such as thin metallic membranes (palladium, vanadium, etc.) and ceramics (perovskites and fluorites), have high selectivity, but low permeability and / or chemical instability [15].

The most common inorganic membranes studied are ceramics, zeolite and silica-based membranes. Ceramic membranes often comprise multiple layers with a macroporous ceramic support coated with a thin layer of ceramic powder dispersed [8], while zeolite (aluminosilicates) membranes are polycrystalline zeolite layers deposited on porous inorganic supports [54]. Both types of membranes are very stable at high temperatures and chemically stable, allowing for

processing of strong solvents or low pH aqueous mixtures [8,54]. Particularly, zeolite membranes offer a good basis as separation material due to their highly ordered well-defined structures, uniform and with molecular-sized pores. Depending on the type of zeolite and cations present, a wide number of different zeolite structures exist and different properties are obtained, as is the case of type A zeolites that form a 3D structure and contain cations that make these membranes very hydrophilic [8].

On the other hand, silica or silica-based membranes comprise another class of inorganic membranes. These membranes are highly selective to permeation of small molecules, are relatively inexpensive and are also quite stable in acidic solutions. However, silica membranes are unstable under high humidity or aqueous conditions, with a gradual decrease of permeability and selectivity. In order to improve the stability of pure silica membrane many researchers have tried to incorporate metal ions into the silica networks and / or increase the hydrophobicity of the organic-inorganic hybrid silica [55].

Mixed matrix membranes are obtained with the addition of selective inorganic fillers into a polymeric matrix, which improves the mechanical properties of the polymeric membrane and reduces the free volume through which molecules may diffuse. They combine the good processability of polymer films with the high selectivity of inorganic materials [8,15].

In order to improve the properties of polymers and enhance their permeability, several approaches and chemical modifications have been proposed, namely: polymer substitution (grafting) or post polymerization substitution; blending with other polymers; incorporation of inorganic materials like silica particles, zeolites and metal organic frameworks (MOFs) [27,56]. The easiest and most feasible approaches involve the incorporation of inorganic materials, named mixed matrix membranes, and blending, because they are easier to be adopted and scaled up for membrane production [47]. However, there are still some drawbacks in the preparation of mixed matrix membranes mainly due to difficulties in obtaining a homogeneous distribution of particles in the polymer matrix [57].

Mixed matrix membranes using zeolites, functionalized carbon nanotubes or magnesium oxide as fillers have been studied for ethanol dehydration, since these membranes showed higher selectivities and/or fluxes than pure polymers [27]. Metal organic frameworks (MOFs) can be another alternative, since the size, shape and chemical capacities of the MOF cavities can be easily adjusted in the polymeric structure by choosing the appropriate linker-metal couples. However, until now, a limited number of studies with MOFs has been carried out [27].

Liquid membranes are divided in two configurations: supported and unsupported liquid membranes [58]. In the supported form there are Immobilized Liquid Membranes (ILM), usually called Supported Liquid Membranes (SLM), and Contained Liquid Membranes (CLM), which depend on the way the support is wetted by the liquid [58,59].

Liquid membranes show great potential, due to the low capital cost involved, high selectivity, low space requirement and low energy consumption. Moreover, they show high efficacy as transport

carriers and higher diffusivities when compared with solid membranes. However, liquid membranes present some relevant drawbacks, namely the lack of adequate long-term stability since the liquids have tendency to evaporate, to dissolve in the phase of contact and / or to get out of the pores [58,59].

The most used membranes in dehydration processes by pervaporation and vapour permeation are polymeric membranes, dominating the membrane separation market [15,39]. With the growing environmental concern and the need to replace petroleum-based materials, it is very important to obtain polymers from renewable sources and many efforts have been devoted to the development of new membranes with high separation performance and reliability. These membranes should present a good compromise between flux and selectivity and also chemical and mechanical stability, when compared with commercial membranes [60]. Among the polymers available, biopolymers are promising materials for this purpose [61].

2.5 Biopolymers

The biopolymers can be divided in categories depending of the production method or origin: (i) biopolymers extracted from biomass, such as polysaccharides (starches, pectins, chitosan, gums, etc.) and proteins or lipids (gelatin from animals sources and soya, as well as, corn fibre from plant sources); (ii) biopolymers obtained by microbial fermentation, such as polyhydroxyalkanoates (PHA), pullulan and bacterial exopolysaccharides; and (iii) chemical synthetized biopolymers obtained from renewable bio-based monomers, such as polylactic acid (PLA) [61–63].

Among the available biopolymers, polysaccharides are the most used industrially in several applications (food, pharmaceutical, medical, etc.). They are commonly extracted from natural resources, such as algae and higher plants, or extracted through chemical hydrolysis or fermentation [64]. The polysaccharides obtained from natural resources depend on the climate conditions and seasons, being the quality and availability of these polysaccharides very variable. As alternative, microbial polysaccharides are good candidates, since their production can be easily controlled, it is possible to obtain high production rates (in days, instead of months, as happens in the case of plants), they do not depend on climate conditions and can be produced from industrial wastes, used as carbon source [62,64,65].

According to the location of polysaccharides in the cell, microbial polysaccharides can be grouped in: cytosolic polysaccharides (responsible for carbon and energy source of the cell), lipopolysaccharides and peptidoglycans (polysaccharides that constitute the cell wall) and exopolysaccharides (EPSs) (polysaccharides that are released out of the cell wall). The latter can also be classified as: homopolysaccharides, which have a single type of monosaccharide (dextran or levan), and heteropolysaccharides (xanthans or gellans), which present several types of

monosaccharides, are complex and more common among the exopolysaccharides produced by bacteria and, moreover, are repeating units synthesised inside the cell [64].

Microbial polysaccharides offer enormous opportunities in different areas, as membrane-based products and processes, due to their high molecular structure variability, which provides them different properties. Though, there are few membranes based on microbial polysaccharides used industrially [60]. The high costs associated to production, namely the cost of carbon source and the cost of bioproduction under sterile cultivation conditions, limit their use in membrane processes [60,64].

2.5.1 Biopolymers in ethanol dehydration by pervaporation

Among the biopolymeric materials that have already been tested for ethanol dehydration by pervaporation, polysaccharides and, in particular, chitosan and sodium alginate have received much attention, due to their good selectivity and high flux [8,46,66–68].

Although they show an excellent affinity for water, they have poor mechanical properties and may present instability in aqueous solutions [69]. Thus, polymer cross-linking and incorporation of particles in the polymer matrix have been used to produce membranes with enhanced water resistance and water selectivity.

The crosslinking degree affects flux, selectivity and membrane stability. A decrease of water permeability is expected with increasing crosslinking, but an improved selectivity and long-term stability can be achieved.

To compare the performance of the different membranes reported in literature, the following parameters will be used: total flux (J_t) (equation 1), separation factor (equation 2); pervaporation separation index (PSI) – equation 3, and selectivity ($\alpha_{water/i}$) equation 4.

$$J_t = \frac{m_{perm}}{A \times t} \quad (1)$$

$$Separation\ factor = \frac{yw/_{yi}}{xw/_{xi}} \quad (2)$$

$$PSI\ (\frac{kg}{m2.h}) = J_t \times separation\ factor \quad (3)$$

$$\alpha_{water/i} = \frac{Pw}{Pi} \quad (4)$$

Where A is the membrane area, m_{perm} is the mass obtained in the permeate (kg), t is the time of experiment (s); y and x are the molar fractions of the components water (w) and organic solvent (i) in permeate and feed, respectively; and P is the permeability of the membrane for water (w) and organic solvent (i).

The fluxes and separation factors depend from the operating conditions of the experiments (feed concentration, permeate pressure and feed temperature), which do not translate the intrinsic properties of the membranes. Hence, the use of permeabilities (P), permeances (P/l; where the l is the thickness membrane) and selectivities ($\alpha_{i/j}$) are related to the intrinsic properties of the membranes, which are more useful to compare effectively the transport properties of the different membranes [70].

Table 2.1: Pervaporation of ethanol solutions with 10 wt.% of water in the feed using membranes obtained from biopolymers.

Active layer	T (ºC)	J_{total} (kg/m^2.h)	Separation factor (-)	PSI (kg/m^2.h)	$\alpha_{water/i}$ (-)	Reference
BC[1]/NaAlg[2]	30	0.12	96	-	-	Suratago *et al.* (2015) [71]
NaAlg crosslinked GA[3]	60	0.30	-	-	1000	Shao & Huang (2007) [46] refers to [72]
NaAlg crosslinked Al^{3+} Cr^{3+}	70	0.94	-	-	2750	Shao & Huang (2007) [46] refers to [73]
HA[4]/NaAlg/PAN[5]	80	0.97	1130	-	500	Gao *et al.* (2014) [74]
CS[6] crosslinked GA	50	1.10	-	-	6000	Shao & Huang (2007) [46] refers to [75]
NaAlg/CS crosslinked GA	60	0.21	-	-	1000	Shao & Huang (2007) [46] refers to [76]
BC	30	0.11	285	32.7	-	Dubey *et al.* (2002) [77]

[1]BC – bacterial cellulose; [2]NaAlg – sodium alginate, [3]GA – glutaraldehyde; [4]HA – hyaluronic acid; [5]PAN – polyacrylonitrile; [6]CS – chitosan.

Chitosan and sodium alginate membranes using glutaraldehyde or ionic cross-linking with multivalent metal ions (e.g. Ca^{2+}, Al^{3+}) were obtained, by suppressing excessive swelling. Blends or self-assembly of layer-by-layer polyelectrolyte polymers, such as chitosan, as polycation, and hydroxyethylcellulose, cellulose acetate and cellulose sulphate, as polyanion polymers, were used and the membranes demonstrated an excellent dehydration performance (Table 2.1). Using 10 wt.% of water in the feed, the selectivity towards water ranges from 500 to 6000 and the total fluxes are always higher than 100 g/m^2.h for all kind of aqueous solution referred in literature [8,69,72].

Regarding membranes for pervaporation using microbial biopolymers there is, so far, not much work published. Bacterial cellulose membranes, for example, have been used for ethanol dehydration and for feed compositions containing less than 50 % water; the selectivity towards water was in the range of 40 to 287. However, a 'trade-off' relationship between selectivity for water and its flux is observed. With an increase in feed water concentration from 10 to 50 %, the flux increases from 112 to 153 g/m^2.h and water selectivity decreases from 287 to 40. This phenomenon is due to the plasticizing effect of water, and probable flow coupling between water and ethanol. As the water concentration in the feed increases, the amorphous regions of the membrane swell and the polymer chains become more flexible, allowing alcohol molecules also to pass through, thus lowering the ability of the membrane for selective transport [77].

2.5.2 Biopolymers in gas dehydration by vapour permeation

Polymeric membranes are the most used to remove water vapour from gas streams in several applications, such as dehydration of natural gas, drying of compressed air, flue gas dehydration, dehydration of organic compounds and steam recovery [39].

Biopolymers are rarely used, according to literature, being drying of compressed air the application where biopolymeric membranes, namely cellulose acetate, are most commonly used, since they present an adequate selectivity for H_2O/N_2 [16,36]. According to Mulder (1996) [78] cellulose acetate membranes have a selectivity of 24000 for H_2O/N_2 and a water permeability of 6000 barrer. In 2007, Park *et al.* [79] described the use of biodegradable chitosan/clay nanocomposite membranes for N_2 dehumidification.

Recent reports refer the use of chitosan membranes for air dehumidification. In the study of Li *et al.* (2015) [80], they synthesized hybrid chitosan membranes using LiCl as inorganic additive and achieved a water permeability of 50000 barrer. Also in 2015, Kudasheva *et al.* [81] developed three types of biopolymeric membranes mixed with LiCl (silk fibroin, chitosan and DNA-Na membrane), and found that the best membrane was the silk fibroin with a water permeability of 58842 barrer. Another work of Li *et al.* [82] in 2014, studied the effect of the addition and removal of glycerine in the structure of chitosan membranes and achieved a water permeability of 55000 barrer for the best membrane developed.

Although the studies for gas dehydration using membranes obtained by biopolymers are relatively few, being the air dehumidification the most cited application, biopolymeric membranes show high potential for gas dehydration. An example is the work developed by Chen *et al.* (2015) [83] using membranes of cellulose acetate for purification of natural gas. These membranes presented, in a mixture of CH_4 and water vapour, a water permeability of 22500 barrer and a selectivity of approximately 103000.

Chapter 3

3 A NEW MICROBIAL POLYSACCHARIDE MEMBRANE FOR ETHANOL DEHYDRATION BY PERVAPORATION

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The author was involved in planning and performing all experiments, discussion and interpretation of the results and preparation of the manuscript.

To facilitate the explanation of the different exopolysaccharides used to prepare membranes, they were called GalactoPol and FucoPol. In this chapter, the EPS corresponds to GalactoPol.

3.1 Summary

In this study, a new microbial exopolysaccharide (EPS) membrane obtained from a low cost and abundant carbon source, the glycerol by-product of the biodiesel industry, was used for ethanol dehydration by pervaporation. Two types of membranes were prepared: homogeneous membranes obtained directly from the fermentation broth and crosslinked with trichloroacetic acid (EPS), and composite membranes with a thin film of crosslinked EPS supported in polyethersulfone (EPS-PES).

These membranes were characterised in terms of their morphological structure, resistance to solvents and mechanical properties. They show a high affinity towards water, good chemical resistance towards organic solvents and adequate mechanical properties.

Pervaporation experiments were performed using both types of membranes for different water concentration in the feed stream (5.0 to 10.0 wt.%) at a constant temperature of 30 ºC. The membranes developed, in particularly the composite EPS-PES membrane, exhibit a high potential for ethanol dehydration, since a water/ethanol selectivity of 3000 at 5.0 wt.% water concentration in the feed was achieved.

Considering the good results obtained, these new membranes will be also evaluated for the dehydration of other industrially relevant solvents, for separation of polar and non-polar compounds in organic mixtures, and also for solvent-resistant nanofiltration processes.

3.2 Introduction

Solvent dehydration processes have a high economic and environmental relevance in the pharmaceutical, fine-chemistry and chemical industry. Among the available techniques for solvent dehydration, hydrophilic pervaporation has gained a progressive recognition due to its relative simplicity and relative low energy input, as compared to traditional energy-intensive methods [49]. Additionally, pervaporation is able to resolve solvent-water azeotropic mixtures, which cannot be easily achieved by traditional distillation processes, and require the use of entrainers, leading to higher costs and complexity. Particularly, the dehydration of alcohols by hydrophilic pervaporation has been studied intensively, representing by far the main industrial application of pervaporation [8,32,84].

The process of hydrophilic pervaporation involves three sequential steps: selective sorption of water from the feed solution to the membrane, diffusion of water/solvent through the membrane and desorption at the permeate side [78]. Transport through a non-porous membrane is usually explained by the sorption equilibrium of the feed components and by the mobility of the permeating compounds across the membrane. Therefore, if the selective transport of a target solute from the feed stream is aimed, it is necessary to assure that the membrane presents a good compromise between flux and selectivity for the target solute, as well as high mechanical and chemical stability for the target application [85–87]. Hydrophilic polymers, such as poly(vinyl alcohol) (PVA), poly(acrylic acid) and polyacrylonitrile have been selected, among others, as membrane materials for the dehydration of various solvents [8,88–90].

Nowadays, with the growing environmental awareness, it is becoming progressively relevant the development of membranes from renewable resources, namely using biopolymers produced from agro-industrial by-products. This approach will present several environmental and economic advantages in the long-term, reducing the impact of low-value agro-industrial wastes and transforming them into valuable materials. On the other hand, non-renewable resources, including petroleum resources, are becoming more expensive, therefore alternatives are needed for polymer production [91,92].

Several authors have proposed the use of biopolymers for solvent dehydration by pervaporation using polysaccharide based membranes, such as chitosan and sodium alginate [93–95]. These polymers are commonly extracted from natural resources and the availability and quality of the biopolymer sources depend from climate conditions and season of the year, which leads to variability of the polymer quality.

Microbial polysaccharides represent a better alternative, since the production parameters can be easily controlled and high production rates can be obtained. However, the high cost of most carbon sources studied, in particularly sugars, has a high impact on the production costs, limiting the potential use of those microbial polymers [65]. Therefore, attention has been directed to the search for viable low-cost carbon sources, namely industrial and agro-industrial by-products.

Recently, it has been reported that by-product streams containing glycerol, from biodiesel production, could be directly applied as carbon source for the production of a new extracellular polysaccharide (EPS), using *Pseudomonas oleovorans*, with attractive productivity and polymer yield. This new EPS is a high molecular weight ($4.6x10^6$ g/mol), negatively charged heteropolysaccharide, composed by sugars (68% galactose, 13% glucose, 17% mannose and 2% rhamnose) and acyl groups (3%), such as pyruvil, succinyl and acetyl [96].

It was also demonstrated that this polymer can be used for producing films which are insoluble in most common organic solvents (actually they revealed to be insoluble in all solvents tested, namely ethanol, isopropanol, dichloromethane, acetone, ethyl acetate and tetrahydrofuran). Moreover, when cross-linked with appropriate agents, these polysaccharide films become insoluble in aqueous solutions while maintaining their resistance to organic solvents. In addition to their structural advantages, these membranes have an important economic advantage because they can be produced by bacteria that use glycerol, an abundant and low cost carbon source [97].

This work is focused on the development and characterisation of homogeneous membranes of EPS obtained directly from the fermentation broth and, also, of composite membranes prepared by casting a thin-film of EPS in a porous support of polyethersulfone (PES). The EPS-PES composite membranes were developed in order to provide a higher flux of the target solute – water, while keeping the selectivity of the separation process. Additionally, it is aimed to obtain membranes with adequate mechanical properties for use under industrial operating conditions.

The membranes developed were characterised in terms of their structure, by optical and scanning electron microscopy (SEM), and their interaction / resistance to different organic compounds and water, by determining their swelling degree. The mechanical properties of the different materials involved – homogeneous EPS membrane, polyethersulfone support, and composite membrane of PES-EPS – were also evaluated.

Finally, pervaporation experiments were performed using ethanol solutions with different water contents (from 5.0 to 10.0 wt.%), typically in the concentration range of interest for ethanol dehydration. The results obtained are interpreted and compared with other biopolymer membranes and with commercial membranes.

3.3 Experimental

3.3.1 Materials

The PES membrane, used as support of the composite membrane, was obtained from Gelman Sciences SB-6407 (USA). This membrane presents a nominal pore size of 0.45 μm, positive charge (1.15 μeq/cm^2) and area of 17.35 cm^2. The commercial PERVAP® 4101 membrane, commonly used for ethanol dehydration, was provided by Sulzer Chemtech (Switzerland). Isopropanol (99.9%), ethanol (99.8%) and ethyl acetate (99.9%) were purchased from Panreac

Química SA (Spain). Dichloromethane (99.9%) was obtained from Fluka Riedel-de Haën (Germany) and Sigma-Aldrich Chemie GmbH (Germany), respectively. Tetrahydrofuran (THF) (99.8%) was obtained from Merck (Germany). Acetone (99.8%) was purchased from Valente e Ribeiro Lda. (Portugal). Molecular sieves 4 Å (8-12 mesh), used to dry the solvents prior to the swelling experiments, were purchased from Sigma-Aldrich Chemie GmbH (Germany). Trichloroacetic acid (TCA), used to crosslink the EPS membranes, was obtained from Merck (Germany).

3.3.2 Membrane preparation

Two types of membranes were prepared: homogeneous membranes of exopolysaccharide (EPS) produced by fermentation of *Pseudomonas oleovorans*, and composite membranes of EPS casted on a polyethersulfone (PES) support.

The EPS homogeneous membranes were prepared directly from the fermentation broth diluted with deionised water (1:2 v/v), followed by cell separation by centrifugation (13000 rpm, 30 min, 10 ºC). An aqueous solution of trichloroacetic acid (TCA, 100% w/w) 1:10 (v/v) was added to the supernatant and, after remaining 10 min at 4 ºC, a second centrifugation was performed to remove the precipitated proteins. The polymer extraction was accomplished using acetone 1:3 (v/v). The resultant precipitated biopolymer (0.49% dry weight [97]) was collected and immediately dissolved in an aqueous solution of sodium aside (10 ppm) to prevent microbial growth. The membrane was cast in a Teflon plate and dried at 30 ºC during 48 h.

The composite EPS-PES membranes were prepared by the deposition of four EPS layers on a PES support, following a procedure similar to the one used for preparing the EPS homogeneous membranes. In order to help the spreading of the layers, an increased polymer concentration was used. Particularly, the dilution of the fermentation broth with deionized water was of 1:1 (v/v), instead of 1:2 (v/v) as in the case of the homogeneous membrane. Each layer has an amount of approximately 5 g by total area of membrane prepared, and it was allowed to dry for 6 h at 30ºC, before adding the next layer.

3.3.3 Membrane characterisation

3.3.3.1 Morphological structure

3.3.3.1.1 Scanning electron microscopy (SEM)

The morphological structure of the membranes was acquired by scanning electron microscopy (SEM) at 10 kV with a Jeol JSM-7001F, Field Emission scanning electron microscope.

3.3.3.1.2 Optical microscopy

The optical microscope (Axioplan 2ie imaging, Zeiss, Germany) was used in order to measure the thickness of the membranes (homogeneous and composite membrane of EPS, and composite PERVAP® 4101), without exposing them to vacuum conditions required by SEM technique. For the homogeneous membrane and for the composite membrane visible light in dark field and amplification of 50 were used. And, for the composite PERVAP® 4101 membrane UV light and amplification of 50 were used.

3.3.3.2 Solvent resistance and swelling behaviour

Small square pieces of homogeneous membranes of EPS (2 cm x 2 cm) were dried during 24 h at 70 ºC. After this procedure the membranes were weighed with a digital balance (KERN ABJ, Germany).

Then, the membranes were immersed in selected organic solvents (ethanol, ethyl acetate, isopropanol, dichloromethane, acetone, tetrahydrofuran (THF)) and water for 24 h at room temperature (24.6 ± 1.1 ºC). In order to ensure that the organic solvents were completely dried, molecular sieves were used to adsorb water from these solvents before each experiment. After this procedure, the membranes were taken out and the excess of solvent was removed from their surfaces using tissue paper and weighed. The degree of swelling for each membrane was determined by equation 1:

$$Swelling_w\ (\%) = \frac{W_f - W_i}{W_i} \times 100 \qquad (1)$$

where W_f, and W_i are the weights of the swollen and dry membranes, respectively.

In all experiments, the membranes kept their integrity and no dissolution to the contacting solvents was apparent.

3.3.3.3 Mechanical properties

These studies were performed in order to characterise the potential behaviour of the membranes under study when exposed to the operating conditions in a pervaporation module.

Mechanical properties such as tensile strength and elongation at break were measured using a TA-Xtplus texture analyser (Stable Micro Systems, Surrey, England). The tensile stress at break is defined as the force that is required to break the films and the elongation at break is calculated

as the percentage increase in length that occurs before the film breaks under defined tension conditions.

The membranes were placed between the grips and stretched at a rate of 0.5 mm/s in tension mode. All mechanical tests were performed at 22.0 ± 2.0 ºC in two different conditions, which aimed to mimic the environment of the membrane before and after being used in pervaporation experiments: membrane samples were equilibrated during 4 days at 44.3% relative humidity (common atmospheric conditions); they were also immersed during 24 h in a solution of 10.0 wt.% water in ethanol. At least three samples of each membrane were used for each test.

3.3.4 Sorption experiments

Membranes with a known mass were immersed in pure deionised water and also in pure ethanol (99.8%) for 24 h at 25.0 ± 0.5 ºC. After this period, it could be considered that the membranes were in equilibrium with the contacting media. The membranes were then removed and weighed after the excess of solvent was removed with tissue paper. The increase in membrane weight is due to the water or ethanol sorbed by the membrane. In order to determine accurately the amount of water and ethanol sorbed, the membranes were heated in a control mode using a thermogravimetric balance (TGA-50) at 39.3 ± 0.9 ºC, and the mass loss was recorded along time. The sorption coefficients of water and ethanol were obtained in g_i/g wet membrane.

3.3.5 Pervaporation experiments

Pervaporation experiments were carried out for both types of membranes, using the experimental setup shown in Fig. 3.1.

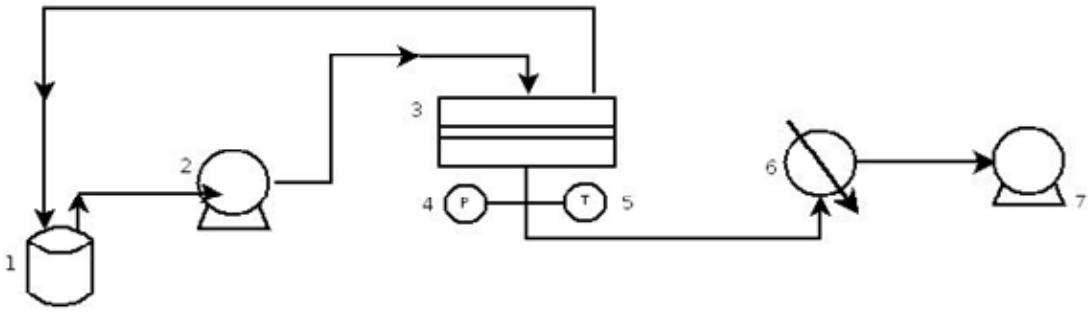


Fig. 3.1: Pervaporation (PV) experimental set-up: 1 – closed stirred feed vessel; 2 – recirculation pump; 3 – flat circular pervaporation module; 4 – pressure transducer; 5 – temperature sensor; 6 – condenser with liquid nitrogen; and 7 – vacuum pump.

This experimental setup consists essentially of a closed feed vessel, a flat circular pervaporation module, a condenser and a vacuum pump (Edwards RV12, UK). The feed vessel was closed and operated with a small headspace. It has a relatively large volume (600 ml) to membrane area ratio, in order to minimize ethanol depletion from the feed during each experiment (which was experimentally confirmed to be lower than 0.2 wt.%). A heating bath (Julabo EH,Germany) connected to the feed vessel was used to keep the temperature of the feed solution constant at 30.0 ± 0.3 ºC. The feed solution was pumped by a recirculation pump (Gilson Minipul S3, USA) to the pervaporation module (flat circular cell) at a flow rate of 22 ml/min. The surface area of the membrane in contact with the feed mixture was 7.54 cm^2. The temperature of the pervaporation module was maintained constant by a heating belt (RKC CB100, Japan) at 30.0 ± 0.1 ºC. A cold trap immersed in liquid nitrogen was used to collect the permeated vapour. The vacuum at in the downstream circuit was 0.9 ± 0.1 mbar obtained by the vacuum pump.

Different concentrations of water in the feed solution were studied (5.0 wt.% and 10.0 wt.% for the homogeneous membrane, and 5.0 wt.%, 7.5 wt.% and 10.0 wt.% for the composite membrane). Each experiment lasted 9 h for the homogeneous membrane. For the composite membrane each experiment lasted only 6 h, because the amount of permeate recovered was large enough to be analysed.

3.3.6 Analytical methods

3.3.6.1 Gas chromatography analysis

The concentration of ethanol in the permeate was determined by gas chromatography (GC, CP-3800, Varian, USA) using an auto sampler (Combi PAL, CTC Analytics, Switzerland). The samples were injected into the gas chromatograph using the technique of static headspace. Specifically, 1 g of sample was heated for 10 min at 70 ºC in vials hermetically sealed, followed by the injection of 1 ml of headspace sample in the gas chromatograph. The injector temperature was 170 ºC and the FID (flame ionization detector) temperature was 250 ºC. The split ratio used was 10. The carrier gas was Helium and the standard deviation for the different compounds examined was found to be always lower than 5%. The column temperature was programmed as follows: 35ºC during 5 min followed by an increase of temperature of 10 ºC/min until 215 ºC [98].

3.4 Results and discussion

3.4.1 Membrane characterisation

3.4.1.1 Membrane structure

The top layer surface and the cross-section views of the homogeneous membrane of EPS and the composite membrane of EPS-PES are shown in Fig. 3.2.

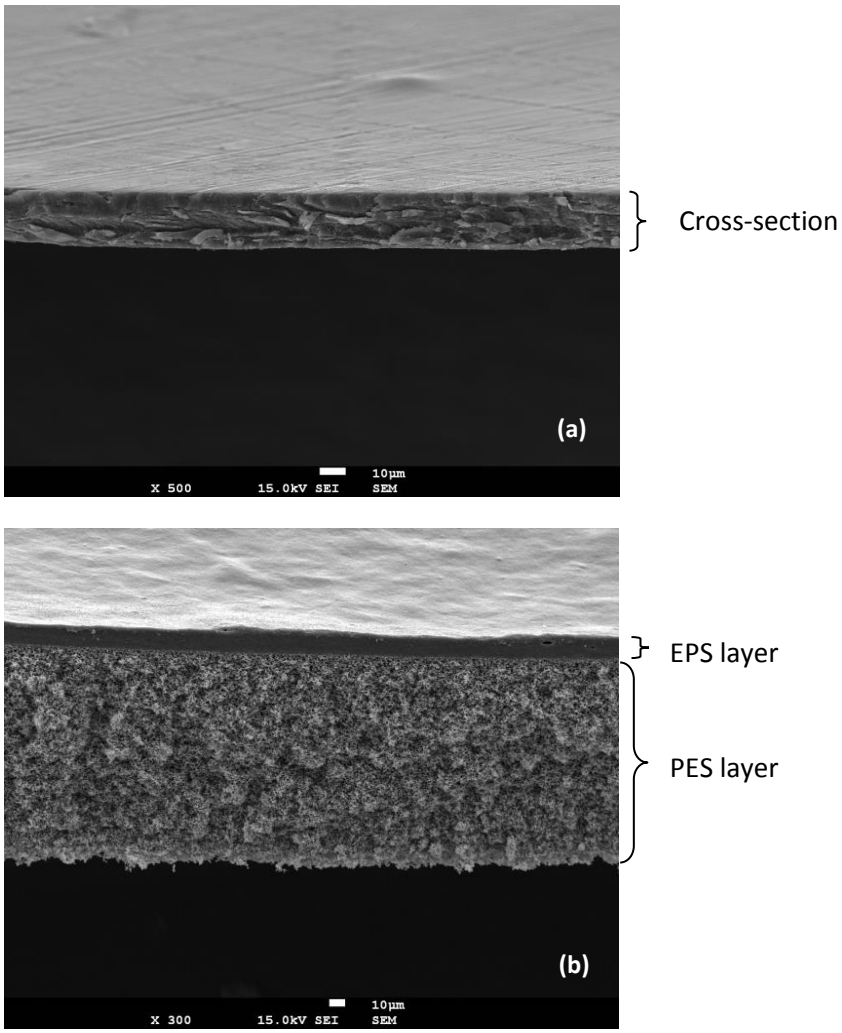


Fig. 3.2: SEM views: (a) cross-section image of an EPS homogeneous membrane; and (b) cross-section image of a EPS-PES composite membrane.

The homogeneous membrane image shows a dense surface without defects. The cross-section image of the composite membrane shows the porous support of PES and the dense top layer of EPS (also without noticeable defects). It can also be noticed that there is a perfect separation and yet a good adhesion, between the layers of EPS and of the support of PES.

In order to determine the thickness of the membranes, without the vacuum effect present during the analysis by SEM, they were also visualized by optical microscopy. Particularly, the thickness of the membranes was obtained through an optical microscopy image analysis using the AutoCAD® software program. It was found that the homogeneous membranes present a thickness of 17.9 ± 3.4 µm, and the composite membranes present a total thickness of 164.5 ± 2.8 µm, from which 12.5 ± 0.4 µm correspond to the thickness of the active layer.

The active layer of the PERVAP® 4101 was also measured by optical microscopy and a thickness of 3.5 ± 0.1 µm was obtained.

3.4.1.2 Solvent resistance and swelling behaviour

These experiments were performed with selected solvents, commonly used in diverse industrial applications, and water (see Table 3.1). As mentioned, in all experiments performed, the membranes kept their integrity and no relevant dissolution to the contacting solvents was apparent. This behavior of the films in water might be unexpected, since the films were produced through dissolution of the EPS in water. However, it was reported that the addition of TCA in the purification step lowered the pH of the solution, promoting the formation of strong interactions between polymer chains and making the membranes resistant to liquid water. Crosslinking reactions are taking place only during the drying process, because polymer molecules are driven to closer contact, as water evaporates [97].

Table 3.1: Swelling results of the homogeneous membrane of EPS at 23 ± 1 ºC.

Solvent	***"Swelling"* (wt.%)**
Acetone	-5.3
Ethyl acetate	-1.3
Ethanol	2.4
THF	2.8
Isopropanol	7.2
Dichloromethane	9.3
Water	95.9

From the increase of membrane weight, after contact with each solvent, it may be inferred if a given solvent presents a high affinity towards the membrane and solubilizes within its polymeric structure.

From Table 3.1 it may be concluded that the homogenous membrane exhibits a negligible swelling when in contact with most solvents, being isopropanol and dichloromethane the organic solvents that promote a higher swelling. The negative swellings observed in the case of acetone and ethyl acetate were due to a minor leaching of the membrane. Considering the low value obtained for ethanol and the high swelling observed for water (swelling of 2.4 wt.% and 95.9 wt.%, respectively for ethanol and water), it may be concluded that this membrane exhibits a high relative affinity for water, which suggests a potentially good behaviour for the selective transport of water against ethanol.

The low degree of swelling in the presence of most organic solvents also suggests that this membrane may be extremely stable when in contact with these solvents. Also, it may be expected

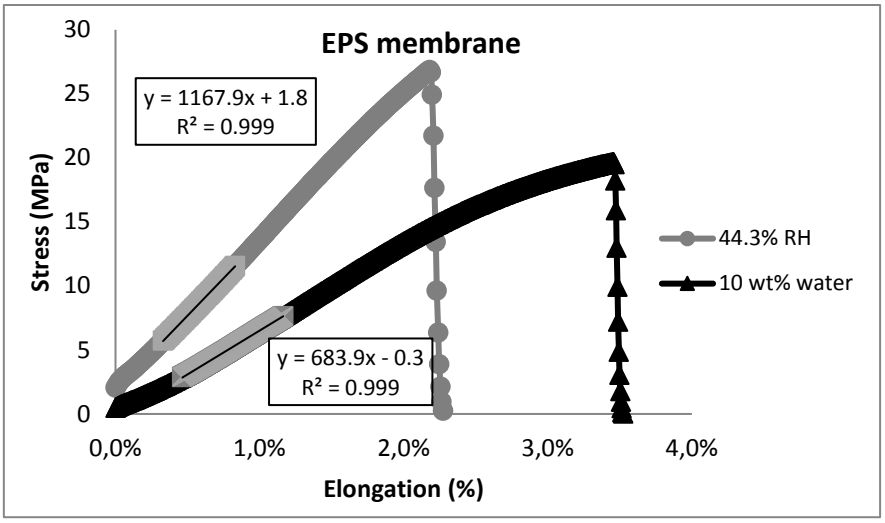
a low permeation of these solvents through the membrane, making it a good candidate for solvent dehydration.

3.4.1.3 Mechanical properties

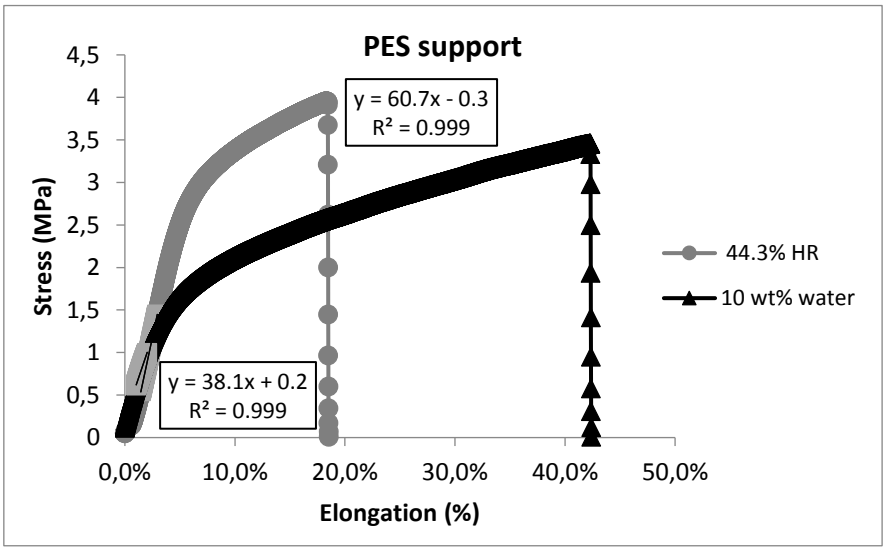
Mechanical strength tests were carried out for the two types of membranes, homogeneous EPS and composite membrane of EPS-PES, and also for the porous PES supporting membrane. Two different experimental conditions were selected in order to: mimic the exposure of these materials to ambient conditions, by equilibration with air with a relative humidity of 44.3% at 22 ºC; and mimic conditions similar to the ones occurring during ethanol dehydration, by immersion during 24 h in a solution of 10.0 wt.% water in ethanol.

Tensile stress studies were performed, instead of compressive stress tests, because the former reflect better the situation of a membrane during operation when assembled in a pervaporation module. Fig. 3.3 shows a sample of stress-elongation curves obtained with these materials. Representing the stress as a function of elongation (%), it is possible to obtain the Young's modulus by determining the slope in the linear region, as shown in Fig. 3.3.

a)



b)



c)

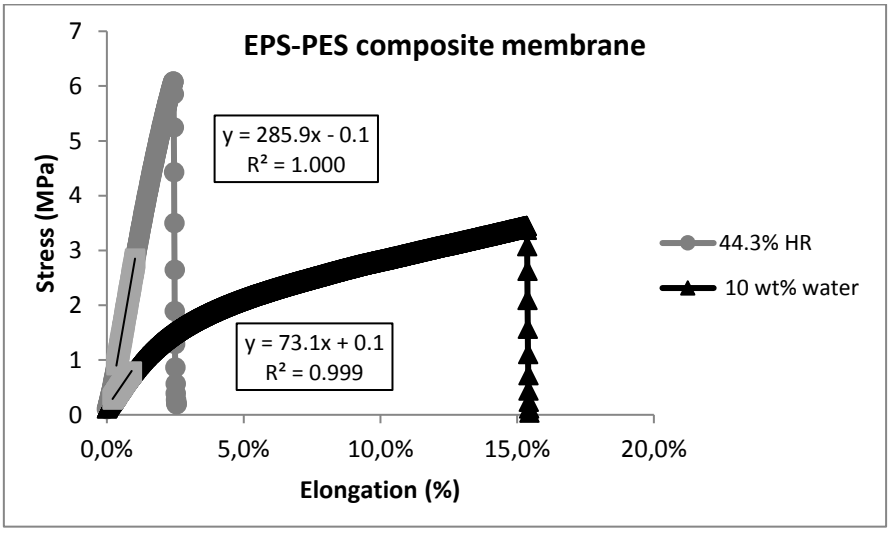


Fig. 3.3: Representative stress-elongation curves and Young's modulus (slope of linear equations inside boxes) of the various materials exposed to air with 44.3% relative humidity at 22 ºC and immersed in 10.0 wt.% water in ethanol solution: (a) EPS membrane; (b) PES support; and (c) EPS-PES composite membrane.

The stress at break relates with the ability of the material to resist rupture when a tension force is applied, and the elongation at break is the elongation recorded at the moment of rupture of the specimen, expressed as a percentage of the original length. Furthermore, the Young's modulus describes tensile elasticity, or the tendency of an object to deform along an axis when opposing forces are applied along that axis. A high Young's modulus refers to a material with a low tensile elasticity. The results obtained are summarised in Table 3.2.

Table 3.2: Average values obtained for the mechanical properties of the membranes developed and for the PES supporting material, for the two experimental conditions studied: exposure to air with 44.3% relative humidity at 22 ºC and immersion in 10.0 wt.% water in ethanol solution.

Membrane	Conditions	Stress at break (MPa)	Elongation at break (%)	Young's modulus (MPa)
EPS	44.3% RH	28.7 ± 2.6	2.4 ± 0.3	1275 ± 150
	water 10.0 wt.%	19.7 ± 0.0	2.8 ± 1.0	991 ± 430
PES support	44.3% RH	3.5 ± 0.4	18.9 ± 4.4	59 ± 3
	water 10.0 wt.%	3.4 ± 0.1	35.1 ± 10.2	52 ± 20
EPS-PES	44.3% RH	6.8 ± 1.6	3.5 ± 1.3	254 ± 20
	water 10.0 wt.%	2.8 ± 0.6	14.7 ± 4.7	60 ± 20

Analysing Table 3.2 and Fig. 3.3 it can be observed that the homogeneous EPS membrane exhibits, for both environmental conditions tested, a behaviour that reflects a higher resistance to rupture and a lower elasticity than the PES support material. As it can be seen, the EPS membrane presents a significantly higher stress at break (higher resistance to rupture), and a higher Young's modulus and lower elongation at break, which reflect a lower elasticity.

From the data obtained it can be also concluded that, when immersed in the 10.0 wt.% water in ethanol solution, all materials tested exhibit a lower resistance to break and a higher elasticity. These results indicate that the membrane becomes more flexible due to solubilisation of the media components within the polymer matrix, leading to a rearrangement of the polymeric chains and, ultimately, swelling. Similar results were also observed by Zereshki *et al*. (2010) [99] with a composite membrane of poly(lactic acid)/poly(vinyl pyrrolidone).

For the composite membrane two different behaviours were observed, depending on the experimental conditions used. In the case of the membrane exposed to air with 44.3% of relative humidity, it can be observed that this membrane exhibits an intermediate behaviour between the homogeneous EPS membrane and the PES supporting material. The stress at break and the Young's modulus present an intermediate behaviour between the homogeneous membrane of

EPS and PES support, although, the elongation at break is similar to the EPS membrane. When the membrane is immersed in a solution of 10.0 wt.% water in ethanol, the support (PES layer) seems to dominate the mechanical properties of the composite membrane. Since these environmental conditions are similar to the ones a membrane experiences during ethanol dehydration by pervaporation, it may be concluded that the composite membrane developed will present a mechanical behaviour close to a PES membrane, which assures an adequate mechanical performance during operation.

The mechanical properties of EPS membranes developed in this work can be compared with the results for other dense membranes of biopolymers reported in the literature (Table 3.3).

Table 3.3: Comparison of the mechanical properties of dense membranes composed by biopolymers.

Membrane	Stress at break (MPa)	Elongation at break (%)	Young's modulus (MPa)	Reference
EPS	28.7 ± 2.6	2.4 ± 0.3	1242 ± 130	Present study at 44.3% RH
EPS-PES	6.8 ± 1.6	3.5 ± 1.3	254 ± 20	Present study at 44.3% RH
Chitosan	82.4 ± 8.5	5.2 ± 0.9	534 ± 44	Suyatma *et al,* 2004 [100] at 50% RH
Sodium alginate	21.2	6.9	-	Kanti *et al*., 2004 [95]
Chitosan-Sodium Alginate	72.3	6.3	-	Kanti *et al*., 2004 [95]

From Table 3.3 it appears that the EPS-based membranes present one of the highest Young's modulus, which means that these membranes are more rigid.

The values of stress at break for the EPS membrane are similar to the membrane of sodium alginate (28.7 MPa and 21.2 MPa, respectively), but lower than chitosan. These results indicate that the homogeneous membrane presents similar mechanical properties when comparing with other biopolymers referred in literature. It is difficult to establish a thorough comparison with other biopolymers because, in most cases, the mechanical properties were not measured under similar conditions.

3.4.1.4 Pervaporation experiments

The pervaporation results obtained for the homogeneous and composite membranes are presented in Table 3.4.

Table 3.4: Mass fluxes of water and ethanol for the homogeneous membrane of EPS and for the composite membrane of EPS-PES.

Membrane	$[Water]_{feed}$ (wt.%)	J_t (g/m².h)	J_w (g/m².h)	J_{et} (g/m².h)
EPS	5.2	21.7 ± 0.2	18.2 ± 0.1	3.5 ± 0.1
	10.1	59.1 ± 0.4	50.5 ± 0.2	8.6 ± 0.2
EPS-PES	5.2	10.9 ± 0.0(2)	10.8 ± 0.0(1)	0.1 ± 0.0(1)
	7.6	20.5 ± 0.0(4)	20.2 ± 0.0(2)	0.3 ± 0.0(2)
	10.4	39.3 ± 0.2	36.0 ± 0.1	3.3 ± 0.1

From Table 3.4 it can be concluded that both membranes present a high selectivity for water against ethanol. As expected, when the driving force for water transport increases (higher concentration of water in the feed stream), higher fluxes of water are obtained. The comparison between the homogeneous and the composite membrane is more difficult to establish because the top layer of the composite membrane was prepared with a solution with a higher polymer concentration (1.24 g/cm^3, versus 0.72 g/cm^3) leading to the formation of an active layer denser than the homogeneous membrane. For this reason, the fluxes obtained with the composite membrane were lower.

In order to better quantify the performance of these membranes, the permeability and selectivity values must be calculated. Permeability of each feed component may be calculated by considering the solution-diffusion equation [101]:

$$J_i = \frac{P_i}{\delta}(p_{i,feed} - p_{i,perm}) \Leftrightarrow J_i = \frac{P_i}{\delta}(\gamma_{i,feed}\, x_{i,feed}\, p^{sat}_{i,feed} - p_{i,perm}) \quad (2)$$

where i is a target compound (water or ethanol), J is the molar flux (mol/m^2.s), P is the permeability (mol/m.s.Pa), p is the partial pressure (Pa), δ is the thickness of the membrane or dense layer of the composite membrane (m), γ is the activity coefficient of a target compound (-), x is its molar fraction in the feed liquid (-) and p^{sat} is the saturation vapour pressure (Pa).

For the range of compositions studied the saturation vapour pressures at 30 ºC [102], calculated through the Antoine's equation, and the activity coefficients are presented in Table 3.5. The values of the activity coefficients were calculated by the Wilson method, as in [98]. This method allows for calculating values of activity coefficients in the whole range of compositions studied, taking

into account the non-ideality of liquid mixtures due to specific interactions, introducing the concept of local composition [103]. This method was also selected because the values calculated are in agreement with experimental values obtained for water and ethanol at infinite dilution.

Table 3.5: Values of calculated saturation vapor pressure at 30ºC (a) and activity coefficients (b) for water and ethanol.

(a)

Compound	**p_i^{sat} (Pa)**
Water	4276.2
Ethanol	10462.0

(b)

$[Water]_{feed}$ (wt.%)	γ_{et}	γ_w
5.2	1.04	2.33
7.6	1.05	2.15
10.4	1.07	1.98

The permeability values, calculated with equation 2, and the selectivity values (calculated as the ratio between the permeability of water and ethanol) allow for better understanding the intrinsic performance of the membranes under study. These parameters are used to compare the results obtained under different experimental conditions [70]. The results obtained are shown in Table 3.6.

Table 3.6: Comparison of permeability and selectivity values of water and ethanol for the homogeneous membrane of EPS and for the composite membrane of EPS-PES (a) and for other membranes referred in literature (b).

(a)

Membrane	**$[Water]_{feed}$ (wt.%)**	**P_w x 10^{12} (mol/m.s.Pa)**	**P_{et} x10^{14} (mol/m.s.Pa)**	**Selectivity (w-et)**
EPS	5.2	4.3 ± 0.8	4.0 ± 0.8	108
	10.1	7.6 ± 1.5	10.7 ± 2.1	69
EPS-PES	5.2	1.8 ± 0.3	0.0(6) ± 0.0(1)	3000
	7.6	2.6 ± 0.4	0.2(5) ± 0.0(4)	1040
	10.4	3.8 ± 0.6	2.9 ± 0.5	134

(b)

Membrane	$[Water]_{feed}$ (wt.%)	T (ºC)	δ active layer (μm)	P_w x 10^{12} (mol/m.s.Pa)	P_{et} x10^{14} (mol/m.s.Pa)	Selectivity (w-et)	Reference
EPS-PES	5.2	30	12.5	1.8	0.0(6)	3000	Present study
PAAHCl-PVA-PVDF	5.0	70	-	4.7	0.2(4)	1950	Namboodiri & Vane, 2007 [104]
EPS-PES	10.4	30	12.5	3.8	2.9	134	Present study
Sodium Alginate-PVA	10.0	45	1.8	2.5	-	-	Namboodiri & Vane, 2007 [104] refers to [105]
PERVAP® 4101	9.9	30	≈3,5	7.2	1.3	554	Present study

From Table 3.6 (a) it can be observed that, for both membranes developed (homogeneous and composite), the permeability values increased and the selectivity values decreased, with increasing water concentration in the feed. These permeability values may be explained by a rearrangement of the membrane polymer, which becomes more flexible (in line with the decrease of the Young's modulus, see section 3.3.3.3) as the concentration of water in the feed phase increases. A higher concentration of water in the feed leads to a higher concentration of water within the membrane and, therefore, to membrane swelling and higher mobility of the polymer chains. As a consequence, permeability increases and selectivity decreases. Still, it must be stressed the high values of selectivity for water transport against ethanol in range of concentrations relevant for ethanol dehydration.

When comparing the composite membrane with other membranes reported in the literature (Table 3.6 b) it can be observed that the EPS-PES membrane has an extremely high selectivity at 5.0 wt.% water in the feed, which compares favourably with the results reported by Namboodiri and Vane (selectivity of 3000 and 1950 for EPS-PES and PAAHCl-PVA-PVDF, respectively). This comparison should be established with care because these works were not performed at the same temperature. A higher temperature (70 ºC) will favour flux of the EPS-PES membrane but, probably, at the expenses of a decrease in selectivity.

On the other hand, if we compare the composite membrane of EPS with a composite membrane also composed by biopolymers (the sodium alginate-PVA membrane), it can be observed that the

EPS-PES membrane exhibits a higher permeability for water than the sodium alginate-PVA, at 10.0 wt.% water in the feed. However, the commercial membrane of Sulzer (PERVAP® 4101) presents a higher value of water permeability and a lower value of ethanol permeability, at 10.0 wt.% water in the feed. Considering these results it is important to identify the role of sorption and diffusion in the transport of ethanol and water, in order to direct further membrane development efforts in the right direction.

3.4.1.5 Transport of water and ethanol through exopolysaccharide dense membranes

The permeability of a given compound i (P_i) may be expressed as the product between its sorption coefficient towards the membrane (S_i) and its diffusion coefficient within the membrane (D_i):

$$P_i = S_i \times D_i \tag{3}$$

The sorption coefficients of pure liquid water and ethanol, S_i^{pure}, were obtained for the homogeneous membrane and for the active layer of the composite membrane by thermogravimetry. Sorption coefficients for water and ethanol using binary mixtures with the compositions of interest were not experimentally measured but, for the purpose of this discussion, such values are not vital. The values obtained are presented in Table 3.7.

Table 3.7: Sorption coefficients for water and for ethanol, for the homogeneous membrane of EPS and for the active layer of the composite EPS-PES membrane.

Membrane	S_{water}^{pure} ($g_w/(g_{wet\ membrane})$)	$S_{ethanol}^{pure}$ ($g_{et}/(g_{wet\ membrane})$)
EPS	0.443	0.034
Active layer of EPS-PES	0.481	0.058

These results show clearly that water is preferentially sorbed by both membranes, as expected. The denser EPS layer of the EPS-PES composite membrane presents a slightly higher sorption coefficient for water (9% higher), but also a higher sorption coefficient for ethanol (70% higher), than the homogeneous membrane.

Unlike sorption coefficients, diffusion coefficients of ethanol are expected to decrease more significantly than the diffusion coefficients of water in a denser top-layer, since diffusion is related with the size of the molecules. Indeed, since ethanol has a higher molecular mass than water, its diffusion coefficient is expected to be more affected in a more compact membrane. Actually, the permeability results obtained (see Table 3.6 a) show exactly this behaviour, which explains the

higher selectivity of the composite membrane for water transport in comparison with the homogeneous membrane.

If we compare the ratio of sorption coefficients (S_w^{pure}/S_{et}^{pure}) (calculated on a molar basis, from the values shown in Table 3.7 expressed on a mass basis) and the corresponding ratio of permeabilities (P_w/P_{et}), we may draw conclusions about the relative importance of each step (sorption and diffusion). The results obtained can be observed in Table 3.8.

Table 3.8: Ratio between water and ethanol permeabilities and ratio between water and ethanol sorption coefficients, calculated in a molar basis, for both membranes.

Membrane	**$[Water]_{feed}$ (wt.%)**	**P_w/P_{et}**	**S_w/S_{et}**
EPS	5.2	108	33
	10.1	69	
EPS-PES	5.2	3000	21
	7.6	1040	
	10.4	134	

From this table it may be concluded that, for the homogeneous EPS membrane, transport is mainly controlled by the strong affinity of water to the membrane, while the contribution of diffusion to the overall selectivity seems less important. On the other hand, when analysing the values obtained for the composite EPS-PES membrane, it seems clear that the transport process is dominated by diffusion phenomena for a lower water content in the feed stream but, progressively, as the water content is increased in the feed stream, sorption becomes the controlling mechanism.

For the composite membrane the decrease of the diffusion step control with increasing water concentration in the feed, corresponds to a higher plasticization of the polymeric structure, as discussed above, leading to a less hindered and selective diffusion. These results suggest that future developments should be focussed on identifying the optimal degree of cross-linking of the membrane, in order to assure a high diffusion selectivity without compromising the absolute value of water permeability. Additionally, the thickness of the composite membrane should be also optimised in order to guarantee a good membrane permeance without affecting the good chemical and mechanical properties observed.

3.5 Conclusions

This work proposes a new membrane material, obtained from a renewable source, for ethanol dehydration by pervaporation. This microbial exopolysaccharide is produced using a low cost, abundant carbon source, the glycerol by-product of the biodiesel industry, which represents a key economic advantage.

The produced EPS homogeneous membrane, obtained directly from the fermentation broth and crosslinked with trichloroacetic acid, and the composite membranes of EPS with a porous polyethersulfone as support (EPS-PES) were characterised in terms of their morphological structure, solvents resistance and mechanical properties. The membranes showed a high affinity to water, good chemical resistance towards organic solvents and adequate mechanical properties under conditions similar to pervaporation.

These new membranes may become an interesting alternative to commercial hydrophilic pervaporation membranes for the dehydration of ethanol. Particularly, the composite EPS-PES membrane, exhibited a water/ethanol selectivity of 3000 at 5.0 wt.% of water in the feed. Strategies, for further improvement should include optimisation of polymer concentration and cross-linking conditions, in order to improve selectivity for higher concentration of water in the feed stream (10.0 wt.% of water in the feed) without compromising the absolute value of water permeability. The preparation of these EPS membranes will also be optimized in order to render their fabrication more sustainable, namely by eliminating the use of acetone or any other hazardous organic solvent. Additionally, it will be important to evaluate these new membranes in other industrially relevant processes, such as the separation of polar and non-polar compounds in organic mixtures, and also for solvent-resistant nanofiltration processes.

Chapter 4

4 Impact of Biopolymer Purification on the Structural Characteristics and Transport Performance of Composite Polysaccharide Membranes for Pervaporation

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The author was involved in all experiments, as well as, in the discussion and interpretation of the results and preparation of the manuscript.

The exopolysaccharide referred in this chapter is the FucoPol.

4.1 Summary

This study discusses the impact of biopolymer purification – by dialysis and by dia-ultrafiltration – on the properties and transport performance of composite polysaccharide membranes for pervaporation. The composite membranes prepared, using as active layer polysaccharides purified by these two methods, were compared in terms of structure, resistance to solvents, mechanical and transport properties.

Both composite membranes exhibited identical resistance to organic solvents, but presented significant differences in terms of swelling degree and transport selectivity. It was found that these differences may be caused by the shear stress imposed during purification by the dia-ultrafiltration method, which leads to a disintegration of polysaccharide aggregates. As a consequence, denser membranes are obtained, due to smaller polysaccharide aggregates formed, which impact the transport selectivity.

Membranes prepared with polysaccharides purified by dia-ultrafiltration revealed to be the best choice for ethanol dehydration by pervaporation, since a water/ethanol selectivity of 143 for 10.0 wt.% water in ethanol was achieved.

4.2 Introduction

Hydrophilic pervaporation is an attractive process for separation of close-boiling point mixtures, azeotropes and drying of solvents, due to its simplicity and low energy input as compared with traditional methods [8,106]. The highest challenge is the development of pervaporation membranes with good chemical resistance, mechanical stability and durability, exhibiting high selectivity and high permeation rate for the target solute [93]. Biopolymers based on natural polysaccharides extracted from plants, algae and animals, have received special attention due to their unique structures that translate into good selectivity and high permeation fluxes [86,107,108]. Additionally, microbial polysaccharides may present new or improved properties that make them competitive with other natural polysaccharides, as well as with synthetic polymers (e.g. polyvinyl alcohol (PVA)) [60].

The properties of microbial exopolysaccharides depend on the extraction, purification and drying methods; and the most appropriated processes must be selected for each case [60,64,109]. Microbial polysaccharides can be recovered from fermentation broths by chemical methods (e.g., using a cationic exchange resin (CER) or solvent precipitation), by physical extraction (by centrifugation, ultrasonication, microwave treatment or heating) or by a combination of both methods [64]. The most common technique used for polymer recovery is solvent precipitation with ethanol or acetone; however, this technique leads to polymers with low purity and high salt content. Additionally, solvent precipitation is a non-environmental friendly process, with low economic feasibility, due to high costs associated with the solvent and its disposal [64]. On the other hand, filtration techniques are recognized as good candidates for polymer recovery and purification at an industrial scale, since they can be easily operated and scaled-up [110]. Moreover, filtration techniques are regarded as more sustainable, due to their low energy and chemicals consumption requirements [111].

The main objective of this work is the development of highly selective composite polysaccharide membranes, comprising a microbial polysaccharide active layer supported on a polyethersulfone membrane for hydrophilic pervaporation processes. Composite membranes provide higher mechanical stability and higher fluxes when compared to homogeneous membranes due to their thinner top active layer [112,113]. The polysaccharide used in this work is produced by a bacterial culture (*Enterobacter* strain A47) using glycerol, a by-product from biodiesel production, as carbon source [114]. This polysaccharide is composed by fucose, galactose and glucose, presents a high molecular weight (4.19×108 - 5.80×106 g/mol) and anionic character, due to the presence of acyl groups [115].

After biomass removal by centrifugation, the purification of the polysaccharide from the complex supernatant is presented and discussed in this work, using two different filtration approaches: dialysis in a static mode, which allows for polysaccharide purification by a purely diffusional transport, and dia-ultrafiltration involving the convective removal of contaminants (e.g. small peptides, sugars and salts) from the biomass free culture broth. These techniques were used in

order to improve the functional properties of the polysaccharide and to remove impurities that interfere with the membrane-forming ability [116], as well as with their final structural, chemical and transport properties.

The purified polysaccharides obtained by the two processes were used to prepare membranes, which were characterised in terms of morphology, resistance to solvents and mechanical stability. Their transport properties were also evaluated for the dehydration of ethanol by pervaporation, since it is one of the most used industrial applications of pervaporation due to the increasing interest in bio-alcohols as alternative to fossil fuels [117].

In order to understand the different characteristics of the composite membranes obtained with the polysaccharide purified using dialysis and dia-ultrafiltration, the chemical composition, rheological properties and polymer particle size of those polysaccharide solutions were evaluated.

4.3 Material and methods

4.3.1 Materials

Genipin supplied by Comercial Rafer S.L. (Spain) was used as crosslinking agent in the preparation of polysaccharide membranes. The polyethersulfone (PES) membranes with a nominal pore size of 0.45 µm and positive charge from Gelman Sciences SB-6407 (USA) were used as support in the preparation of the composite membranes. Ethanol (99.9%) was purchased from VWR International – Material de Laboratório, Lda (Portugal). Ethyl acetate (99.9%) was purchased from Panreac Química SA (Spain). Dichloromethane (99.9%) and toluene (99.9%) were obtained from Fluka Riedel-deHaën (Germany) and Sigma-Aldrich Chemie GmbH (Germany), respectively. Tetrahydrofuran (THF) (99.8%) was obtained from E. Merck (Germany). Acetone (99.8%) was purchased from Valente e Ribeiro Lda. (Portugal). The sodium hydroxide used to adjust the pH was acquired from Eka (Sweden). Albumin used for calibration of Lowry method was purchased from Merck (USA).

The membranes utilized for dialysis and dia-ultrafiltration were provided, respectively, from Thermo Fisher Scientific (USA), model SnakeSkin® Pleated; and GE Healthcare (USA), model UFP-500-6A.

4.3.2 Methods

4.3.2.1 Extraction and purification of polysaccharides

The protocol used for extraction of extracellular microbial polysaccharides from the fermentation broths involved the following steps: dilution with deionised water (1:4 v/v) to reduce the viscosity; heat treatment during 1 h at 70 ºC in order to inactivate the bacterial cells and enzymes [118], followed by cell removal by centrifugation. The supernatant containing the polysaccharide was

then further purified by dialysis or by dia-ultrafiltration for removal of low molecular weight compounds (e.g. small peptides, salts, glycerol and sugars). The polysaccharide was then obtained by freeze drying the purified supernatant.

The cell free supernatant was purified by dialysis using a 10 kDa dialysis tubing (SnakeSkin® Pleated, Thermo Fisher Scientific, USA) against 5 l of distilled water during 2 days (replaced each day).

In parallel, the cell free supernatant was also purified by dia-ultrafiltration for removal of low molecular weight compounds from the fermentation broth, allowing for their faster removal, when compared with the dialysis process. Dia-ultrafiltration was performed in a tangential flow filtration mode using polyethersulfone hollow fiber membranes with a molecular weight cut-off (MWCO) of 500 kDa. This hollow fiber membrane module had an area of 0.28 m^2 and presented a water permeability of 260 ± 50 l/h.bar.m^2. The diluted polysaccharide supernatant was pumped from the feed tank to the lumen of the hollow fiber membranes. The permeate stream was collected in the shell side and the retentate stream was recirculated to the feed tank. This process was performed with constant addition of distilled water to the supernatant container in order to maintain the feed volume constant, facilitating solute permeation by reduction of concentration polarization effects and membrane fouling. This procedure was carried out at room temperature (23 ºC) and at a constant transmembrane pressure (TMP) of 0.4 ± 0.1 bar.

Each run was performed with 3 l of the polysaccharide fermentation broth. During dia-ultrafiltration, samples of retentate and permeate were collected every 20 min, in order to monitor the retentate conductivity and protein content. When the conductivity reached a value below 200 µS/cm (identified as the value below which the removal of impurities becomes irrelevant), the treated supernatant was concentrated 3 times in the same membrane system, in order to facilitate the freeze drying process of the polysaccharide.

4.3.2.2 Membrane preparation

The membrane forming solutions were obtained by dissolution of 1.5 %w/v of the dried polysaccharide, purified either by dialysis or by dia-ultrafiltration, in distilled water during 12 h. Then, 1 %w/v of genipin was added to the aqueous solution and stirred during 1h, followed by a pH adjustment to 11 using a sodium hydroxide solution (NaOH). Genipin was added in order to promote the crosslinking of the polysaccharide matrix.

The composite membranes were prepared by casting successive layers of the membrane forming solution on a polyethersulfone (PES) porous support (17.35 cm^2). Each layer had an amount of 2 g of polymer solution. The first layer was allowed to dry for 24 h at 30 ºC, before adding the second layer, which was dried in the same conditions.

In addition, homogeneous membranes were also prepared by casting the membrane forming solution in a Petri dish and drying at 30 ºC during 24 h. These homogeneous membranes were

used in order to provide information relative to the dense active layer of the composite membranes (which are identical in structure and chemistry).

4.3.3 Characterisation of the active layer of the composite membranes

4.3.3.1 Hydrophilic character

The hydrophilic character of the membranes was determined from the water contact angles of the homogeneous membrane surfaces. The water contact angles were measured at room temperature (23 ºC) using a goniometer (KSV Instruments LTD, CAM100, Finland) with the software KSV CAM 100.

The contact angle values determined correspond to the average of four measurements performed in different regions of the membrane surfaces.

4.3.3.2 Morphological and chemical characterisation

The morphological and elemental composition of the homogeneous membranes was carried out before and after immersing the membranes in a solution with 10 wt.% of water in ethanol, in order to infer about the membranes stability after contact with the solutions, to be used in pervaporation experiments. Characterisation was performed by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) using a field emission scanning electron microscopy (Jeol JSM7001F, Oxford), with a detector of light elements.

4.3.3.3 Solvent resistance, swelling and leaching analysis

The solvent resistance, swelling and leaching of the homogeneous membranes were analysed as described by Meireles *et al.* [113], using equations 1 and 2, respectively for swelling degree and leaching.

$$Swelling_w\ (\%) = \frac{W_f - W_i}{W_i} \times 100 \quad (1)$$

$$Leaching_w\ (\%) = \frac{W_d - W_i}{W_i} \times 100 \quad (2)$$

where W_f and W_i are the weights of the swollen and dry membranes, respectively. W_d is the weight of the membranes dried at 70 ºC during 24 h after a swelling experiment.

In the present study these properties were analysed upon immersion of the membranes in six organic solvents (ethanol, dichloromethane, acetone, ethyl acetate, toluene and tetrahydrofuran (THF)), during 24 h at 23ºC.

4.3.4 Mechanical properties

In order to characterise the stability of the membranes along the pervaporation process, the mechanical properties of the composite membranes were evaluated in two different conditions: after membrane exposure to air with 48% of relative humidity (RH) (to mimic air conditions before pervaporation tests) and after their immersion for 24h in a solution of 10.0 wt.% water in ethanol (to infer about the stability of the membranes during a pervaporation experiment).

Tensile strength and elongation at break were measured using a TA-Xtplus texture analyser (Stable Micro Systems, Surrey, England) at room temperature (22 ºC). The membranes were fixed with tensile grips and stretched at a rate of 0.5 mm/s in a tension mode. These experiments were conducted at least three times.

4.3.5 Pervaporation experiments

Pervaporation experiments were performed for ethanol dehydration using the two types of composite membranes prepared (with the polysaccharide obtained by dialysis or by dia-ultrafiltration). The experimental setup used was described in a previous study from Meireles *et al.* [113]. Experiments were carried out at constant temperature of 30 ± 0.5 ºC, using a feed solution with 10.0 wt.% of water in ethanol and a membrane with an effective surface area of 7.54 cm^2. The pervaporation driving force was achieved by imposing a vacuum absolute pressure of 1.5 ± 0.2 mbar in the downstream circuit. Each experiment lasted 4 h upon preconditioning the membrane for 30 min. The concentrations of ethanol in the feed solution and permeate were measured by refractive index using an Abbe refractometer (ATAGO CO., Ltd, Japan).

The transport properties of the membranes were quantified in terms of water and ethanol permeabilities and selectivity, in order to understand the intrinsic performance of the membranes under different experimental conditions.

4.3.6 Polysaccharide solutions characterisation

4.3.6.1 Monosaccharide analysis

For determination of the sugar composition, 5 mg of dried polysaccharide was dissolved in 5 ml of distilled water and hydrolysed with trifluoroacetic acid (TFA) (0.1 ml TFA 99%) during 2 h at 120 ºC. Quantification of the constituent monosaccharide monomers in the hydrolysate was obtained by liquid chromatography (HPLC), using a CarboPacPA10 column (Dionex), equipped

with an amperometric detector. This analysis was carried out at 30 ºC, using 4 mM sodium hydroxide (NaOH) solution as eluent, at a flow rate of 0.9 ml/min.

4.3.6.2 Salt content

In order to understand the influence of the dialysis and the dia-ultrafiltration processes in the salt content of the purified polysaccharide solutions before freeze drying, calcium (Ca^{2+}), sodium (Na^{+}), potassium (K^{+}), iron (Fe^{3+}) and magnesium (Mg^{2+}) ions, were quantified by inductively coupled plasma atomic emission spectroanalysis (ICP) equipped with a radio-frequency (RF) generator of 40.68 MHz, a Czerny-Turner Monochromator with 1.00 m (sequential), a AS500 auto sample and data acquisition software.

4.3.6.3 Protein content

The Lowry method was used to analyse the total protein content of the fermentation broth and the polysaccharide solutions purified by dialysis and by dia-ultrafiltration, following the procedure described in [119]. The absorbance was measured at 750 nm (Spectrophotometer Helios Alpha, Thermo Spectronic, UK). Albumin solutions with a concentration range between 0 to 500 mg/l were used as protein standards.

4.3.7 Rheological characterisation

The rheology of membrane forming solutions of polysaccharide purified either by dialysis or by dia-ultrafiltration, was studied. The apparent viscosity and viscoelastic properties of the membrane forming solutions were studied using a controlled stress rheometer (HAAKE MARS III, Thermo Scientific, USA), equipped with a cone and plate geometry (diameter 35 mm, angle 2º). During the experiments, the shearing geometry was covered with paraffin oil in order to minimize sample dehydration. The samples were equilibrated at 25.0 ± 0.1 ºC for 10 min, and flow curves were obtained using a steady-state flow ramp (torque was imposed using a logarithmic ramp) in the shear rate range from 0.001 to 1000 s-1. Frequency sweeps were carried out at controlled stress (0.1 Pa), within the linear viscoelastic region, to measure the frequency dependence of the storage (G') and loss (G'') moduli, before and after steady state tests. At least two replicates were made for each test.

In order to better understand the effect of the shear stress caused by pumping and recirculation on the rheological properties of the membrane forming solutions of polysaccharide, two additional experimental conditions were analysed: (i) dialysis after a previous pumping of the cell free fermentation broth, in order to study the impact of shear stress caused by the pump itself (referred in this work as dialysis R); and (ii) dialysis after circulation of the cell free fermentation broth in

the hollow fiber membrane module (referred here as dialysis M) in order to evaluate the additional effect of shear stress caused by the passage of the feed solution over the membrane – Fig. 4.1.

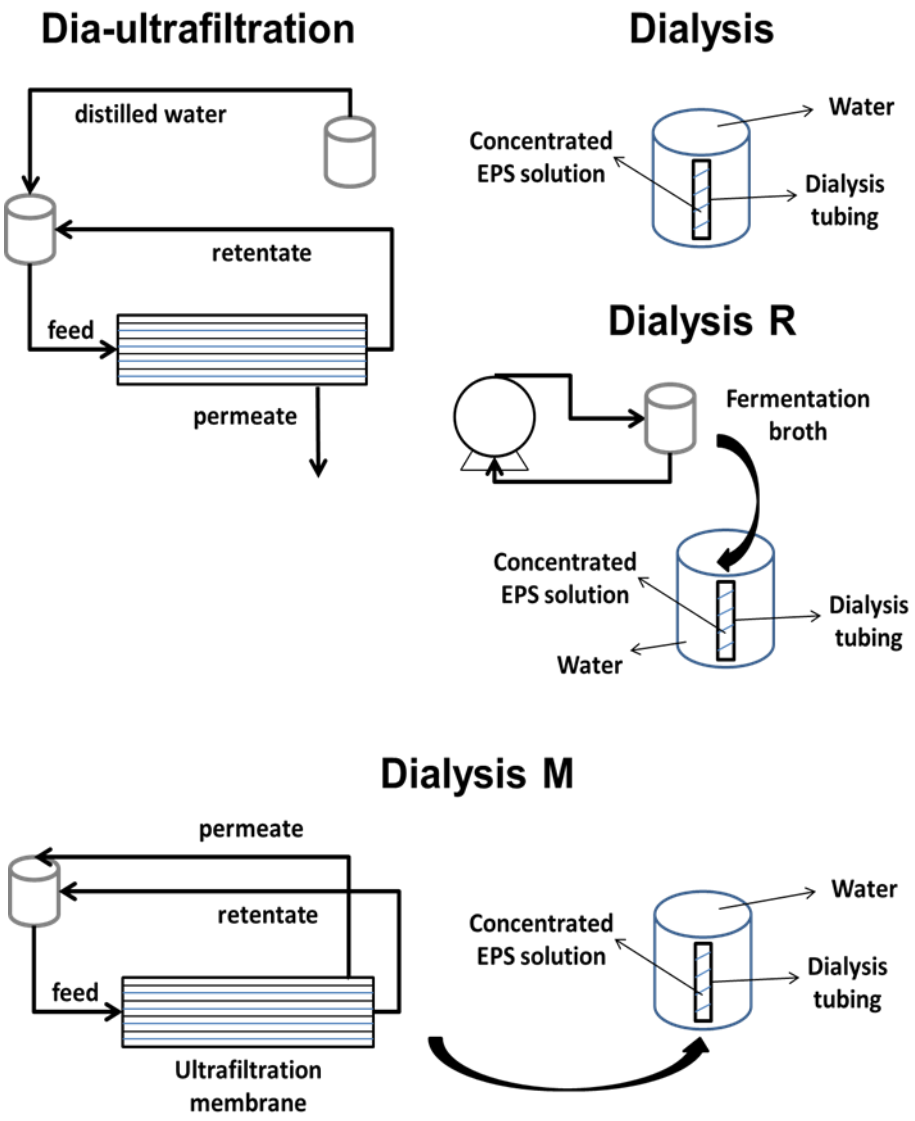


Fig. 4.1: Scheme of the four purification methods used in rheological characterisation.

4.3.8 Polysaccharide particle size characterisation

The effect of the different shear stress conditions in the processes of dialysis and dia-ultrafiltration of the polysaccharide membrane forming solutions was also evaluated through dynamic light scattering (DLS), which allows for characterizing the polysaccharide particle size.

The dynamic light scattering experiments were performed in a Zetasizer Nano Series ZEN3600 (Malvern, UK) operated with a 633 nm laser. The detection used a non-invasive back scattering technique (173º). DLS analysis was performed at constant temperature, at 25.0 ± 0.2 ºC, and a

minimum of five replica measurements was made. Each step of the membrane preparation procedure (polymer dilution, addition of Genipin and so on) was evaluated by DLS. The results are reported as the Z-average mean diameter and represent the average of the values obtained.

4.4 Results and discussion

4.4.1. Characterisation of the active layer of composite membranes

In order to characterise the active layer of the composite membranes, homogeneous membranes were prepared with the polysaccharide purified by dialysis or by dia-ultrafiltration. These homogeneous membranes were characterised in terms of hydrophilic character, chemical and structural properties. Furthermore, their resistance to organic solvents, swelling ability and leaching to contacting organic solvents, were also evaluated.

4.4.1.1 Hydrophilic character

The hydrophilic character of the homogeneous membranes was determined by the analysis of their surface water contact angle. This analysis revealed that both membranes were moderately hydrophilic, exhibiting the same value of water contact angle of approximately 83.0 ± 1.0º, which indicates that the purification method followed to produce polysaccharides does not influence the hydrophilic behaviour of the membranes. The moderate hydrophilicity of both membranes may be due to the presence of Genipin used as crosslinking agent, in agreement with Muzzarelli *et al.* (2009) [120] who found that the addition of Genipin to chitosan films leads to the increase of their water contact angles, increasing the hydrophobic character of the films.

4.4.1.2 Morphological and chemical characterisation

The morphological and chemical characteristics of the membranes were analysed by SEM/EDX. SEM/EDX analysis were performed with membranes exposed to atmospheric conditions (23.0 ºC and 48.0% RH) (A) and with membranes which were in contact to a 10.0 wt.% water/ethanol solution for 24 h (B), in order to mimic the pervaporation conditions. The results are shown in Table 4.1.

Table 4.1: Chemical analysis of the homogeneous membranes using polysaccharides purified by dialysis or by dia-ultrafiltration in two different conditions: (A) exposed at atmospheric conditions and (B) after immersion in a solution of 10.0 wt.% of water in ethanol.

Element	Dialysis		Dia-ultrafiltration	
	A (wt.%)	B (wt.%)	A (wt.%)	B (wt.%)
Sodium (Na)	7.21 ± 0.32	3.14 ± 0.18	4.54 ± 0.20	2.72 ± 0.16
Silicium (Si)	6.24 ± 0.31	5.70 ± 0.24	4.43 ± 0.20	5.17 ± 0.23
Phosphorous (P)	3.58 ± 0.34	1.46 ± 0.20	1.08 ± 0.18	1.16 ± 0.19
Potassium (K)	4.85 ± 0.37	1.97 ± 0.21	4.16 ± 0.23	3.21 ± 0.24
Magnesium (Mg)	0.52 ± 0.20	0.00	0.00	0.00
Calcium (Ca)	2.22 ± 0.35	0.00	0.00	0.00
Chloride (Cl)	0.90 ± 0.32	0.00	0.00	0.00

It can be observed from Table 4.1 that the membranes prepared with the dialysed polysaccharides present a higher salt content (magnesium, calcium and chloride) on the surface than those prepared with the dia-ultrafiltrated polysaccharides. It can also be seen that both membranes suffered a loss of salts when exposed to a solution of 10.0 wt.% of water in ethanol. Actually, after contact with the hydro-alcoholic solution the salt composition of both membranes becomes quite similar. This may be explained by salt leaching from the membrane when in contact with the ethanol solution.

Furthermore, the SEM images revealed that the membranes obtained using the polysaccharide purified by dialysis are more affected by the solution of 10.0 wt.% of water in ethanol, since they show a more heterogeneous surface, possibly due to some surface structure disintegration taking place during their contact with this ethanol solution. On the contrary, the membranes prepared using the dia-ultrafiltrated polysaccharide seem to have less surface heterogeneities after being exposed to the same conditions.

4.4.1.3 Solvent resistance, swelling and leaching analysis

The membranes swelling degree depends on their structure and affinity to different solvents [51,121]. Therefore, the analysis of the membrane swelling behaviour can provide information about the sorption of different solvents in the membrane, which is a relevant information in terms of membrane stability and potential behaviour for transport under pervaporation conditions.

The experiments to determine solvent resistance, degree of swelling and leaching (calculated from equations 1 and 2, respectively) were performed with selected solvents, which may be dehydrated industrially by pervaporation (see Table 4.2).

Table 4.2: Swelling and leaching degree of the homogeneous membranes prepared using the polysaccharides obtained by dialysis or by dia-ultrafiltration.

Solvent	Dialysis		Dia-ultrafiltration	
	Swelling (wt.%)	Leaching (wt.%)	Swelling (wt.%)	Leaching (wt.%)
Ethanol	66.0	-21.9	-1.7	-4.2
Dichloromethane	7.3	-8.6	3.7	-5.7
Acetone	8.3	-7.7	-0.9	-1.3
Ethyl acetate	-0.4	-13.9	1.5	-9.7
Toluene	6.4	-8.2	17.7	0.9
Tetrahydrofuran	-1.6	-8.6	26.1	-11.4

From these experiments, it is possible to conclude that both membranes are resistant to all solvents tested. Still, these membranes exhibit swelling degrees and leaching significantly different, which suggest that these membranes are structurally distinct.

Table 4.2 also shows that the membranes prepared with a dia-ultrafiltrated polysaccharide solution present a higher degree of swelling for toluene and tetrahydrofuran (17.7 and 26.1 wt.%, respectively), while the membranes prepared with a dialysed polysaccharide exhibit a high degree of swelling for ethanol (66.0 wt.%). This high degree of swelling in the presence of ethanol indicates that this membrane has high affinity for this compound and, therefore, it will not be adequate for ethanol dehydration. According to the rheological characterisation performed, the dialysed polysaccharide solution is less viscous and particles with a smaller size are produced,

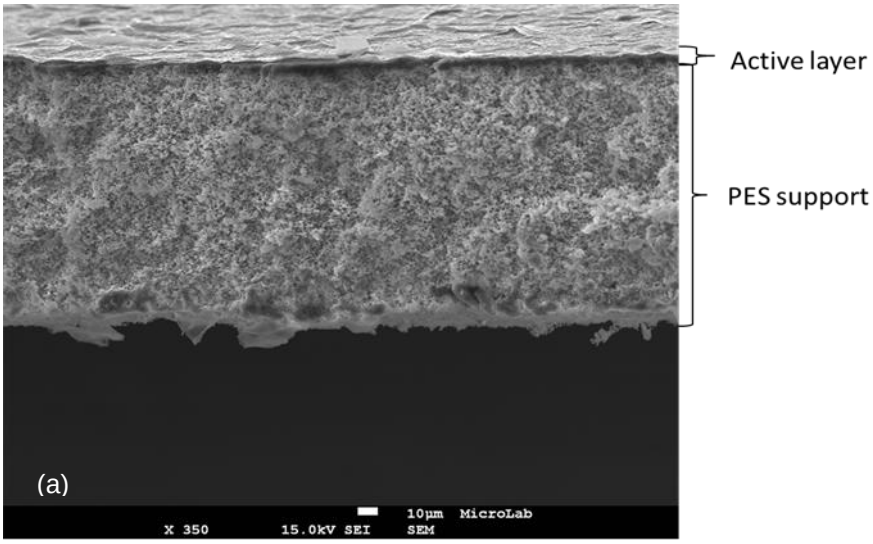
when comparing with the dia-ultrafiltration method. As a consequence, tighter membranes are produced which translates in a higher swelling.

On the other hand, the analysis of the leaching values obtained for the two membranes shows that the membranes purified by dialysis present a higher leaching when compared with the membranes using the polysaccharide purified by dia-ultrafiltration. In the agreement with the EDX analysis, these differences denote that the membranes prepared with the polysaccharide purified by dialysis have a higher structural instability caused by a higher loss of constituents from the polymer matrix (e.g. salts), when contacting different solvents.

4.4.2 Structural and mechanical analysis of composite membranes

The composite membranes were characterised in terms of morphological structure by scanning electron microscopy (SEM). Additionally, determination of mechanical properties was also performed. In order to facilitate the understanding of the text, the composite membrane with an active layer of polysaccharide purified by dialysis is referred as “d/EPS-PES”; the composite membrane with an active polysaccharide layer purified by dia-ultrafiltration is referred as “DU/EPS-PES”.

The cross-sections of the EPS-PES composite membranes obtained by the two purification methods, dialysis and dia-ultrafiltration, are shown in Fig. 4.2.



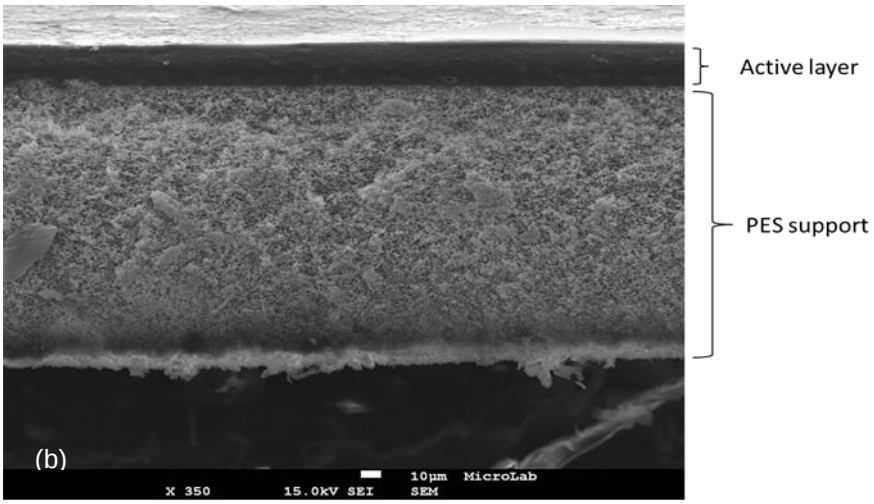


Fig. 4.2: Cross-section images obtained by SEM of the composite membranes prepared from polysaccharide purified by: (a) dialysis and (b) dia-ultrafiltration (magnification of 350 x).

It is possible to see that the polysaccharide forms a dense active layer at the top of both composite membranes. However, the DU/EPS-PES membrane presents a noticeable separation between the two layers, in opposition to the d/EPS-PES membrane. This feature evidences that the film-forming solution of the polysaccharide purified by dialysis was able to penetrate in a certain extent into the pores of the membrane support. This is in agreement with the results obtained by rheological characterisation (see section 4.6.2), that show that the dialysed membrane forming solution is less viscous than the dia-ultrafiltrated membrane forming solution.

SEM images also revealed that the thickness of the active polysaccharide layer depends of the purification method. The active layer of the d/EPS-PES composite membranes presented a thickness of 9.7 ± 3.0 µm whereas the active layer of the DU/EPS-PES composite membranes had a thickness of 21.1 ± 2.7 µm. These thicknesses were also confirmed by measurement with micrometer (Elcometer® 124, UK).

The mechanical properties measurements were carried out for the two types of composite membranes (d/EPS-PES and DU/EPS-PES). Two different experimental conditions were selected: 1 – atmospheric conditions (48% RH and 23 ºC); and 2 – after immersion of the membranes in a solution of 10.0 wt.% of water in ethanol during 24 h, in order to mimic the conditions that the composite membranes are exposed during an ethanol dehydration process. The results obtained are summarized in the Table 4.3.

Table 4.3: Results of mechanical properties (tensile tests) for both types of composite membranes (d/EPS-PES and DU/EPS-PES) in two experimental conditions: atmospheric conditions with a relative humidity (RH) of 48.0% and after immersion for 24 h in a solution of 10.0 wt.% water in ethanol.

Membrane	Conditions	Stress at break (MPa)	Elongation at break (%)	Young's Modulus (MPa)
d/EPS-PES	48.0% RH	4.1 ± 0.0	4.5 ± 0.2	157.2 ± 14.0
DU/EPS-PES		3.1 ± 0.3	2.8 ± 0.4	155.6 ± 51.1
d/EPS-PES	10.0 wt.% water	1.8 ± 0.0(4)	11.4 ± 5.1	51.5 ± 31.3
DU/EPS-PES		2.5 ± 0.2	33.5 ± 7.3	29.1 ± 4.4

According to Table 4.3, it is possible to observe that both membranes have similar stress at break and Young's modulus values when exposed to atmospheric conditions (48% RH), meaning that under these conditions the membranes presented almost the same resistance to deformation.

Under pervaporation mimicking conditions (10.0 wt.% water in ethanol), it is possible to perceive that both membranes tested showed a lower stress at break and higher elongation at break, and a lower Young's modulus when compared with the results obtained under atmospheric conditions. These results show that they become less rigid when submerged in the ethanol/water solution. This fact is attributed to the solubilisation of the media components (water and ethanol) within the polymer matrix, which act as plasticizers, leading to more flexible membranes. Nevertheless, under these conditions the DU/EPS-PES composite membrane exhibited a slightly higher stress at break, higher elongation at break and lower Young's modulus than the d/EPS-PES composite membrane.

From these results it may be anticipated that the DU/EPS-PES composite membrane will present a higher stability under pervaporation conditions, as it handles a higher deformation before rupture.

4.5 Pervaporation experiments

Pervaporation experiments were performed for ethanol dehydration, in order to compare the transport properties of the composite membranes coated with the polysaccharide purified by dialysis and by dia-ultrafiltration (d/EPS-PES and DU/EPS-PES, respectively). The fluxes obtained for both composite membranes are shown in Table 4.4.

Table 4.4: Mass fluxes (total, water and ethanol) of both composite membranes (T=30 ºC; downstream pressure = 1.5 ± 0.1 mbar).

Membrane	$[Water]_{feed}$ (wt.%)	J_t (g/m².h)	J_w (g/m².h)	J_{et} (g/m².h)
d/EPS-PES	10.2	126.9 ± 12.4	75.0 ± 3.7	51.9 ± 16.1
DU/EPS-PES		71.1 ± 2.5	65.4 ± 3.1	5.7 ± 0.5

It is shown that the total mass flux using the d/EPS-PES composite membrane was higher than the DU/EPS-PES composite membrane (126.9 g/m².h and 71.1 g/m².h, respectively). However, the d/EPS-PES composite membrane presented almost the same value of water and ethanol fluxes, which indicates that the d/EPS-PES composite membrane is not adequate for ethanol dehydration. This is in accordance with the results of swelling, since this membrane presented a high affinity for ethanol (see section 4.4.1.3). On the other hand, when comparing the water flux obtained with both membranes, it can be observed that the DU/EPS-PES composite membrane exhibits a water flux approximately 10x higher than that of ethanol. Therefore, the DU/EPS-PES composite membrane seems to be a better candidate for ethanol dehydration, since it allows for a higher selectivity for water transport.

As described in our previous work ([113]), in order to compare these results with others referred in the literature, the permeability and selectivity were calculated using the solution-diffusion model (equation 3). In this way, the contribution of the structure of the membrane in transport performance can be explained and quantified, without the interference of operating conditions [70].

$$J_i = \frac{P_i}{\delta}(p_{i,feed} - p_{i,perm}) \Leftrightarrow J_i = \frac{P_i}{\delta}(\gamma_{i,feed}\, x_{i,feed}\, p^{sat}_{i,feed} - p_{i,perm}) \quad (3)$$

where i is the target compound (water or ethanol), J is the molar flux (mol/m².s), P is the permeability (mol/m.s.Pa), p is the partial pressure (Pa), δ is the thickness of dense active layer of the composite membrane (m), γ is the activity coefficient of the target compound (-), x is its molar fraction (-) and p^{sat} is the saturation vapour pressure (Pa).

The permeability and selectivity values were obtained for both membranes using equation 3. The results obtained are presented in Table 4.5.

Table 4.5: Water and ethanol permeability and selectivity values for composite membranes of polysaccharide obtained by the two purification methods: dialysis and dia-ultrafiltration, referred as d/EPS-PES and DU/EPS-PES, respectively.

Membrane	$[Water]_{feed}$ (wt.%)	P_w x 10^{12} (mol/m.s.Pa)	P_{et} x10^{13} (mol/m.s.Pa)	Selectivity (w-et)
d/EPS-PES	10.2	6.0	3.4	18
DU/EPS-PES		11.9	0.83	143

As shown in Table 4.5, the DU/EPS-PES composite membrane presents a higher water permeability and lower ethanol permeability, which is in agreement with the swelling study results. Therefore, the use of membranes prepared with dia-ultrafiltrated polysaccharide is advantageous for dehydration of ethanol-water solutions.

In order to identify the potential of the DU/EPS-PES composite membrane for ethanol dehydration, this membrane was compared with other membranes referred in the literature (Table 4.6).

Table 4.6: Comparison of the transport properties of the DU/EPS-PES composite membrane with other membranes referred in the literature.

Membrane	$[Water]_{feed}$ (wt.%)	T (ºC)	δ active layer (μm)	P_w x 10^{12} (mol/m.s.Pa)	P_{et} x10^{13} (mol/m.s.Pa)	Selectivity (w-et)	Reference
EPS-PES[a]	10.4	30	12.5	3.8	0.29	134	Meireles *et al.* (2013) [113]
DU/EPS-PES	10.2	30	21.1	11.9	0.83	143	Present work
HA/Alg/PAN[b]	10.0	80	0.5	0.04	0.0024	148	Gao *et al.* (2014) [74]
PERVAP® 4101	9.9	30	≈3.5	7.2	0.13	554	Meireles *et al.* (2013) [113]

[a]EPS-PES – exopolysaccharide-polyethersulfone

[b]HA/Alg/PAN – hyaluronic acid/sodium alginate/polyacrylonitrile

A careful comparative analysis of membrane separation efficiencies should be based on a compromise between water permeability and selectivity. Therefore, when comparing the performances of the DU/EPS-PES composite membrane and EPS-PES membrane (containing an active layer of a different polysaccharide and purified by solvent precipitation with acetone), listed in

Table 4.6, we notice that the two membranes show similar selectivities (143 and 134, respectively for the DU/EPS-PES composite membrane and for the EPS-PES membrane). However, the DU/EPS-PES composite membrane presents a higher water permeability, which has a positive impact on process throughput, without compromising the membrane selectivity towards water.

Also, if we compare the DU/EPS-PES membrane with the HA/Alg/PAN membrane, despite their similar selectivity (143 and 148, respectively), the water permeability is much lower for the HA/Alg/PAN membrane, which translates into a poor throughput.

Finally, when comparing the DU/EPS-PES composite membrane with the commercial membrane PERVAP® 4101, it is possible to perceive that the DU/EPS-PES composite membrane presents a higher water permeability but with a lower selectivity. The higher water permeability of the DU/EPS-PES membrane offers the advantage of a higher throughput (a lower membrane area is required), but a higher loss of ethanol will take place through the permeate.

These results demonstrate that among the membranes used in this comparative analysis the composite membrane developed in the present work is a good candidate for ethanol dehydration.

4.6 Polysaccharide solutions characterisation

In the present study, it was possible to perceive significant differences in the transport performance of the composite membranes using a polysaccharide purified with two different purification methods: dialysis and dia-ultrafiltration. In order to better understand these differences, the chemical composition of the polysaccharide solutions (in terms of monosaccharides, proteins and salts), and, their rheological properties and particle size in the membrane forming solutions were also evaluated.

4.6.1 Impact of purification methods on the chemical composition of polysaccharide solutions

The composition in monosaccharides was analysed for the polysaccharide solutions obtained by dialysis and by dia-ultrafiltration, in order to understand if their chemical composition may explain the different performance of the membranes prepared.

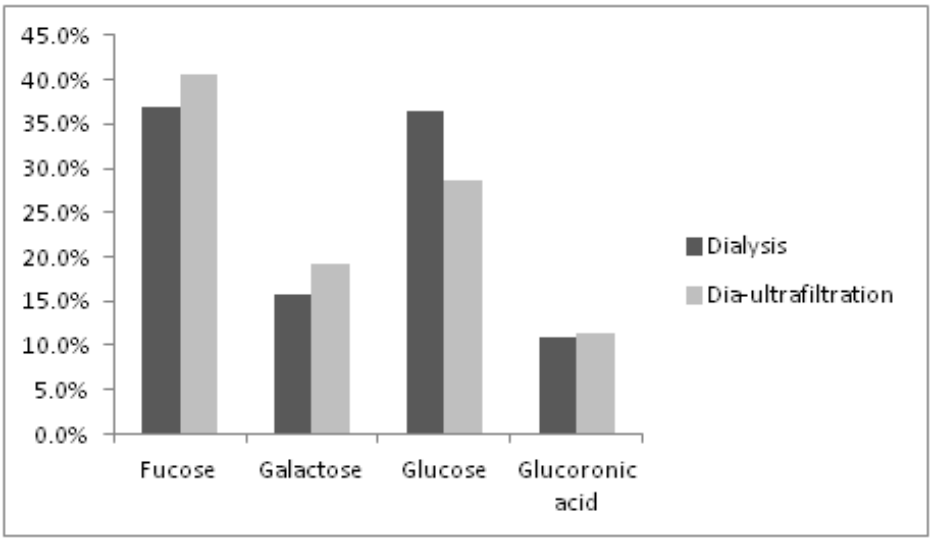


Fig. 4.3: Determination of monosaccharide composition of the polysaccharides obtained by the two purification methods (dialysis and dia-ultrafiltration).

According to Fig. 4.3 the purified polysaccharides obtained by dialysis or by dia-ultrafiltration are composed by fucose, galactose, glucose and glucoronic acid. Furthermore, no significant differences were detected in terms of sugar content, with exception of glucose, whose concentration was higher in the polysaccharide purified by dialysis (36.5% against 28.6%). The only variation was in the ratio Fucose/Glucose which is 1.0 for the dialysed polysaccharide and 1.4 for the polysaccharide obtained by dia-ultrafiltration.

Differences in salt content of dialysed and dia-utrafiltrated polysaccharide were also assessed through quantification of calcium (Ca^{2+}), iron (Fe^{3+}) potassium (K^{+}), magnesium (Mg^{2+}) and sodium (Na^{+}) ions by inductively coupled plasma atomic emission spectroanalysis (ICP-AES).

Table 4.7. Ion content in the polysaccharide solutions purified by dialysis and by dia-ultrafiltration determined by ICP-AES.

Element	Dialysis	Dia-ultrafiltration
Ca^{2+} (mg/l)	0.30	0.04
Fe^{3+} (mg/l)	0.03	0.03
K^{+} (mg/l)	2.83	5.89
Mg^{2+} (mg/l)	0.38	0.34
Na^{+} (mg/l)	6.53	5.33

By the analysis of the ion concentration present in Table 4.7, it is possible to conclude that both purification methods generated a polymer solution with a higher content of sodium (Na^+) and potassium (K^+), when compared to the other elements. However, with the exception of potassium, both purification methods generated a polysaccharide with almost the same concentration of salts in their composition, since the differences were not relevant.

From the protein content in the dia-ultrafiltrated and the dialysed polysaccharide, it was found that the process of dia-ultrafiltration and dialysis removed around 59.0 wt.% and 57.0 wt.% of the total proteins present in the original fermentation broth, respectively. Therefore, it is possible to conclude that both purification methods led to identical protein removal efficiencies, revealing that the differences observed in the behaviour of the two membranes cannot be explained by their protein content.

4.6.2 Rheological characterisation of the membrane forming solutions

In complement to the chemical characterisation (monosaccharide composition, salt content and protein content) a rheological characterisation of the membrane forming solutions was carried out, in order to understand whether the different behaviour exhibited by the two types of composite membranes (d/EPS-PES composite membrane and DU/EPS-PES composite membrane) were caused by the different shear stress conditions that the solutions were exposed during the distinct purification processes. One should note that the shear stress imposed on the polysaccharide solution by pumping and recirculation through the membrane module during the dia-ultrafiltration process is significantly higher than the shear stress conditions inherent to a pure diffusional process, such as dialysis. For this reason, four membrane forming solutions, obtained in different conditions, were analysed: (i) dia-ultrafiltration; (ii) dialysis after a previous passage of the cell free fermentation broth through the pump and hollow fiber membrane module used in the dia-ultrafiltration, operated in total recirculation mode (dialysis M); (iii) dialysis with a previous pump recirculation of the cell free fermentation broth (dialysis R); and (iv) only dialysis – see Fig. 4.1. The results obtained are presented in Fig. 4.4.

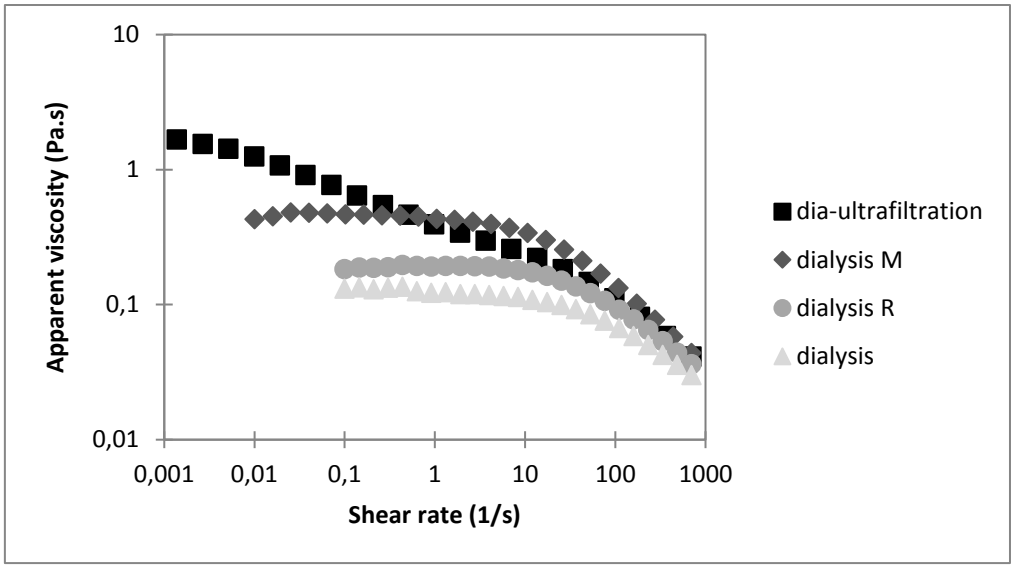


Fig. 4.4: Flow curves of the membrane forming solutions using the polysaccharide obtained with four different purification methods: dia-ultrafiltration; passage of the cell free fermentation broth through the pump and hollow fiber membrane module followed by dialysis (dialysis M); dialysis after a previous pump recirculation of the cell free fermentation broth (dialysis R); dialysis.

As observed in Fig. 4.4, the dia-ultrafiltration method produced a membrane forming solution with higher apparent viscosity at lower shear rate values. It was also verified that all methods involving pumping and recirculation led to a higher viscosity of the membrane forming solution when compared to dialysis in a “static mode”. This result suggests that the shear stress caused by pumping and recirculation led to the disintegration of polysaccharide aggregates improving the dispersion degree of the polymer chains in solution, conducting to an increase of the solutions viscosity. This is in agreement with the study of Xu *et al.* (2014) [122] who noticed that mechanical stress could reduce the size of the agglomerates and disaggregate the larger bundles into small units. In addition, the better dispersion of polymer chains in solution created a more compact polymeric matrix upon membrane formation by solvent evaporation.

The results of the frequency sweep tests of the membrane forming solutions using the polysaccharide purified by the four different methods are shown in Fig. 4.5.

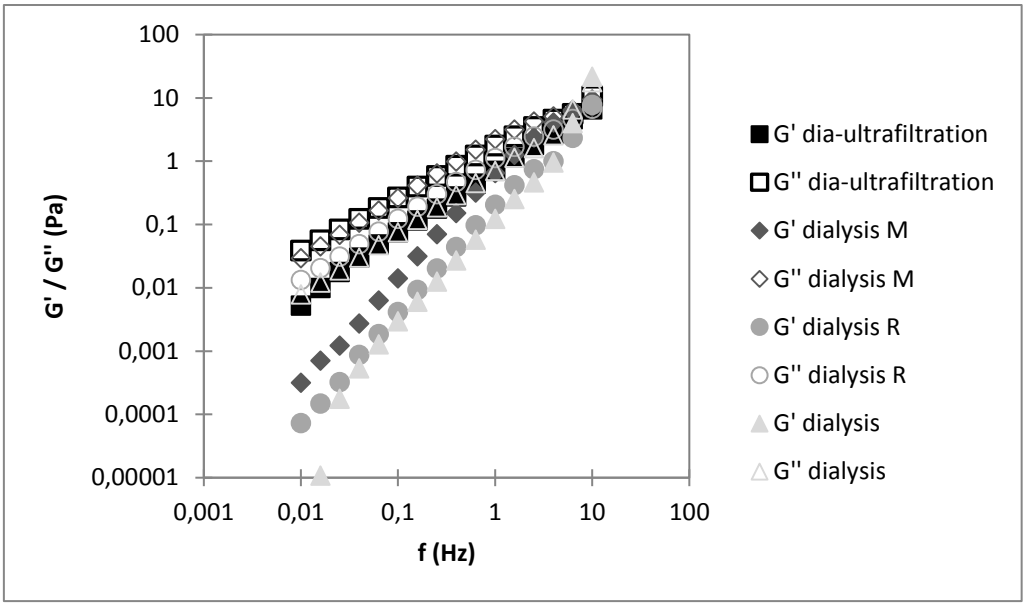


Fig. 4.5: Mechanical spectrum of the membrane forming solutions obtained from four purification methods: dia-ultrafiltration; passage of the cell free fermentation broth through the pump and hollow fiber membrane module followed by dialysis (dialysis M); dialysis after a previous pump recirculation of the cell free fermentation broth (dialysis R); dialysis.

The results presented in Fig. 4.5 show that all membrane forming solutions exhibited typical viscous fluid properties with the viscous modulus (G'') higher than the elastic modulus (G') in the entire range of frequency studied, except at higher frequencies where a cross-over was achieved. This fact shows that the polysaccharide obtained with all purification methods shows a viscous behaviour constituted by entangled polymer chains without strong interactions.

4.6.3 Polysaccharide particle size characterisation

In order to confirm the results obtained in the rheological characterisation, dynamic light scattering (DLS) measurements were carried out aiming at determining the polysaccharide aggregate size and evaluate the influence of each membrane preparation step on polysaccharide aggregation. The first step (1) refers to the polymer (polysaccharide dialysed or polysaccharide dia-ultrafiltrated) diluted in distilled water; the second step (2) is the addition of the crosslinking agent, Genipin, to the polysaccharide solution; the third step (3) analyses the effect of pH change from 6 to 11, through addition of a solution of NaOH to the membrane forming solution; and, finally, the fourth step (4) evaluates the effect of solvent evaporation by increasing the temperature to 30 ºC. The values obtained are represented in Fig. 4.6.

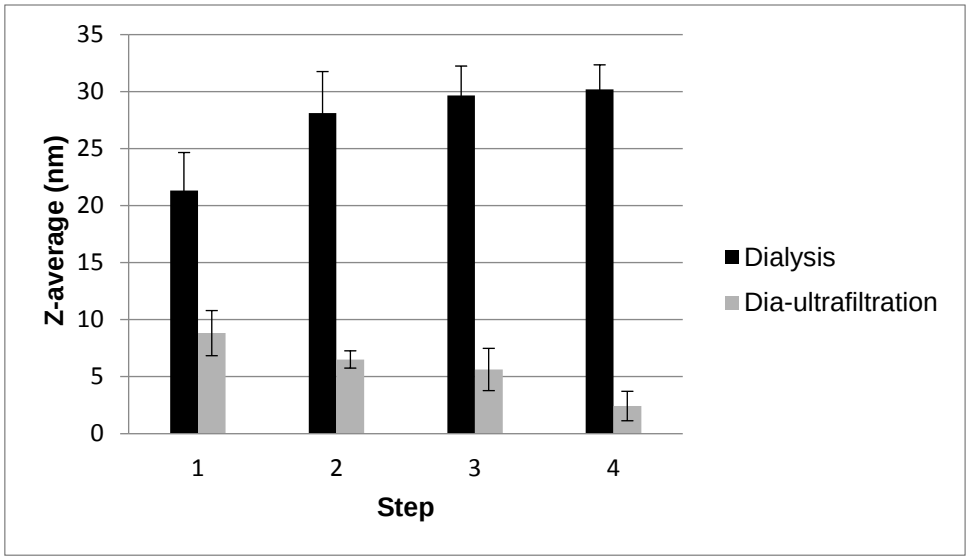


Fig. 4.6: Z-average of polysaccharide aggregates in each step of membrane preparation with the polysaccharide solutions from dialysis and dia-ultrafiltration method. Step 1 – polysaccharide dissolved in distilled water; Step 2 – addition of Genipin; Step 3 – pH change; and Step 4 –temperature increase to 30 ºC.

Analysing the Z-average results (Fig. 4.6), it is possible to observe that the polysaccharide obtained by dialysis and dia-ultrafiltration show a completely different particle size. The Z-average particle size obtained in step 1 for the solution of dialysed polysaccharide and dia-ultrafiltrated polysaccharide were respectively 21.3 ± 3.3 nm and 8.8 ± 2.0 nm. Furthermore, it was also observed that the particle size of dialysed and dia-ultrafiltrated polysaccharide polymeric solutions exhibited opposite behaviour along the different membrane preparation steps. Similar membrane preparation procedures induce an increase of the particle size for the dialysed polysaccharide solution whereas a decrease of the particle size for the dia-ultrafiltrated polysaccharide solution was observed. These results evidence that the process of membrane formation led to a disintegration of polysaccharide aggregates in the case of the polysaccharide purified by dia-ultrafiltration, in contrast with the polysaccharide aggregation that occurred during membrane formation using the dialysed polysaccharide. These results are in agreement with the rheology experiments which showed that the shear stress caused by pumping and recirculation in the dia-ultrafiltration method determines the formation of smaller aggregates, when compared with the dialysis method. Furthermore, the mean diameter of the particle size decreased when the polymer purified by dia-ultrafiltration was crosslinked (8.8 ± 2.0 nm and 6.5 ± 0.8 nm, respectively before and after the addition of the crosslinking agent), which suggests that the polymer chain distension induced by the dia-ultrafiltration facilitates the covalent crosslinking, by promoting a tighter packing of the polymer chains. A similar result was reported by Zhang *et al.* (2014) [123], where crosslinking also led to a decrease of the mean diameter of the filled hydrogel particles of pectin and caseinate.

From these studies, it is possible to conclude that small aggregates led to the formation of tighter membranes, exhibiting enhanced transport selectivity, mainly attributed to the low ethanol permeability, as shown by the results obtained for ethanol dehydration by pervaporation.

4.7 Conclusions

In the present work the influence of two purification methods, dialysis in a static mode and dia-ultrafiltration in a tangential flow filtration mode was evaluated.

Composite membranes prepared with a polysaccharide purified by these methods were characterised in terms of morphology, chemical and mechanical stability, and transport performance for ethanol dehydration by pervaporation.

The membranes developed using the polysaccharide purified by dia-ultrafiltration showed to be more adequate for ethanol dehydration, since they exhibited a high water/ ethanol selectivity. The dia-ultrafiltrated membrane forming solution showed a higher apparent viscosity and the presence of smaller polysaccharide aggregates, due to the shear stress caused by pumping and recirculation imposed in the dia-ultrafiltration process, when compared to the membrane forming solution of dialysed polysaccharide. This shear stress conditions induce a better dispersion of the polymer chains in solution, leading to a tighter membrane, with a better transport performance.

Further improvement of the membranes obtained by dia-ultrafiltration should include the optimization of the thickness of the active layer of the composite membranes in order to improve the long term stability of the membranes and promote higher fluxes, without compromising selectivity.

Chapter 5

5 Development and Characterisation of Hybrid Polysaccharide Membranes for Dehydration Processes

Submitted as: Inês T. Meireles, Rosa M. Huertas, Cristiana A.V. Torres, Isabel M. Coelhoso, João G. Crespo, Development and characterisation of hybrid polysaccharide membranes for dehydration processes, Carbohydrate Polymers (2018).

The membrane preparation for all the experiments presented was developed by Rosa M. Huertas, as well as, the interpretation of the results of TGA, DSC and FT-IR analysis. The biodegradability experiments were performed in collaboration with Cristiana A.V. Torres.

The author was involved in all experiments, as well as, in the discussion and interpretation of the results, and preparation of manuscript.

5.1 Summary

The purpose of this work is the development and characterisation of new hybrid polysaccharide (FucoPol) membranes. These membranes were prepared by incorporation of a SiO_2 network homogeneously dispersed by using a sol-gel method with (3-Glycidyloxypropyl) trimethoxysilane (GPTMS) as a crosslinker silica precursor. These membranes were further crosslinked with $CaCl_2$ for reinforcement of mechanical properties and improvement of their permeation performance. The membranes were characterised in terms of their structural, mechanical and thermal properties.

They presented a dense and homogeneous structure, resistant to deformation, with a glass transition temperature (Tg) of 43 ºC and a thermal decomposition between 240-251 ºC.

In order to evaluate their potential for dehydration processes, the membranes were tested for ethanol dehydration by pervaporation and also for gas (nitrogen) dehydration. They exhibited high water selectivity values, similar to the commercial membrane PERVAP® 4101, however they lost their stability when exposed to solutions of 10.0 wt.% water in ethanol. In contrast, the hybrid FucoPol membranes developed were stable when applied in N_2 dehydration, leading to reproducible performance and very high water selectivities.

5.2 Introduction

Dehydration of organic solvents, in particular ethanol dehydration, is the most important application of pervaporation [8]. In this process, hydrophilic membranes are used due to their high selective for water. However, they may present poor mechanical stability in the presence of high water content [124]. Therefore, several efforts have been devoted to enhance membrane stability, using different strategies, such as crosslinking, chemical modifications, use of polymer blends and development of organic-inorganic hybrid membranes, among others [124].

Hybrid membranes have become an important research topic in membrane science because they combine the easy processing and low-cost of polymeric membranes with the high permeation fluxes and mechanical properties of inorganic membranes [125,126]. Due to their unique characteristics, they have been recognized as promising membrane materials for several applications, such as pervaporation and gas separation. [127,128]. Although these hybrid membranes generally exhibit enhanced permeability and selectivity compared to purely polymeric membranes, their fabrication usually involves some difficulties, namely agglomeration of inorganic particles or leaching of the particles out of the membrane due to the poor compatibility between the polymeric matrix and the inorganic particles [125,129]. Among the available techniques to prepare hybrid membranes, the sol-gel process has been extensively used to provide chemical bonding between the organic and the inorganic phases, allowing the inorganic phase to disperse homogenously in the polymeric matrix and control the concentration of precursors employed [125,130].

In the last years, the preparation of hybrid membranes using polysaccharides as polymer matrix has been increasing [124,131,132]. However, it is necessary to take into account the compatibility of polysaccharides in terms of solubility, pH and hydrophilicity to perform the sol-gel process, in order to obtain homogeneous materials [133]. On the other hand, in order to control the rate of degradation and mechanical properties, and avoid the excessive swelling during dehydration of solvents by pervaporation, covalent bonds are necessary. Thus, the use of silica precursors with cross linkable and favourable functional groups may increase the membrane stability, changing the polymer structure and leading to better performing membranes [134]. In particular, (3-Glycidyloxypropyl) trimethoxysilane (GPTMS) has been explored as one of the most commonly used organic silanes that form covalent bonds between organic and inorganic networks [135]. The three hydrolysable alkoxy groups and high reactive epoxide ring present in GPTMS can create covalent bonding with the hydroxyl groups of polysaccharides, leading to a SiO_2 network. Peng *et al.* (2006) [136] reported that poly(vinyl alcohol) (PVA) + GPTMS hybrid membranes exhibited improved transport properties for the separation of benzene/cyclohexane mixtures. Also, Pandis *et al.* (2014) [137] found an improvement of the mechanical properties of chitosan + TEOS (tetraethylorthosilicate) + GPTMS hybrid membranes. Other works reported the use of hybrid polysaccharide (chitosan, alginate or cellulose) membranes for alcohol dehydration by pervaporation, using different inorganic materials, such as graphene oxides [138,139], silica particles [140,141] and titanium particles [142].

The purpose of this work is the development and characterisation of a new hybrid polysaccharide membrane, using GPTMS as precursor of a sol-gel reaction, and the exopolysaccharide – FucoPol – produced by *Enterobacter* A47 [2]. The chemical, thermal and mechanical properties of the membrane developed are analysed, as well as its morphological structure, swelling and biological degradability. These membranes were then applied for ethanol dehydration by pervaporation and also for gas (nitrogen) dehydration, in order to evaluate their potential for dehydration processes.

5.3 Experimental

5.3.1 Materials

(3-Glycidyloxypropyl) trimethoxysilane (GPTMS) purchased from Sigma-Aldrich (USA) and acetic acid glacial (99-100%) purchased from J.T. Baker (USA), were used as precursor and acid catalyst, respectively, in the sol-gel process. Calcium chloride ($CaCl_2$) (>93.0 %) was obtained from Fluka Analytical (USA) and ethanol absolute (99.99 %) was obtained from Fisher Chemical (USA). Magnesium nitrate hexahydrate (98.0 %) was supplied by Alfa Aesar (UK). Nitrogen (99.99 %) and helium (99.99 %) used in gas dehydration tests were obtained from Irmasolda (Portugal).

5.3.1.1 Polysaccharide production and purification

FucoPol was produced by *Enterobacter* A47 using glycerol as carbon source, in a 10 L bioreactor with controlled temperature (30 ºC) and pH (7). The bioreactor was operated in a batch mode (initial glycerol concentration of 40 g L^{-1}) during the first 10 h of cultivation, followed by a fed-batch mode for 3 days (feeding with a 200 g L^{-1} glycerol solution at a rate of 20 g L^{-1} h^{-1}). The aeration rate (0.125 vvm, volume of air per volume of reactor per minute) was kept constant throughout the cultivation, while the dissolved oxygen (DO) concentration was controlled by automatic variation of the stirrer speed (300-800 rpm), provided by two six-blade impellers. DO was maintained below 10 % during the fed-batch phase [143].

FucoPol extraction and purification consisted on several steps as described in Ferreira *et al*. (2014) [62]. At the end of the cultivation run, the culture broth was diluted (1:5 v/v) to reduce its viscosity. The diluted broth was centrifuged (8875 G, during 30 min) to remove bacterial cells. The supernatant that resulted from the centrifugation was submitted to a thermal treatment (70 ºC, 1 h) to guarantee the inactivation of bacterial enzymes. Then, it was centrifuged (8875 G, during 30 min) again, to remove precipitated proteins and remaining cells. After this procedure, the supernatant was submitted to a dia-ultrafiltration process, using a crossflow membrane cassette (Hydrosart Ultrafiltration Cassettes, Sartorius Stedim Biotech GmbH, Germany) with a molecular weight cut-off of 100 kDa and a surface area of 0.6 m^2, operated at a transmembrane pressure of 0.4 bar, to remove low molecular weight contaminants, e.g. salts, glycerol and

proteins. After removal of impurities, the treated supernatant containing FucoPol was concentrated 5 times, using the same membrane module, switching to an ultrafiltration processing mode. The solution obtained was freeze dried (Martin Christ, model Epsilon 2– 40, Germany) during 48 h.

This FucoPol polymer was found to have a sugar composition of 37.0 %mol of fucose, 34.0 %mol of glucose, 23.0 %mol of galactose and 6.0 %mol of glucoronic acid, obtained by liquid chromatography (HPLC) using a CarboPacPA10 column (Dionex) as described in our previous work [144].

5.3.2 Membrane preparation

Five membranes with different calculated amounts of silica precursor (eq.1 and 2) were prepared as described by Huertas *et al.* (2014) [145], to obtain final concentrations of SiO_2 (3.0, 5.0, 7.0, 7.5 and 8.0 w/w%) and a molar ratio between GPTMS SiO_2 precursor and glacial acetic acid glacial of 2.6:1.

$$m_{SiO_2} = \frac{x\ SiO_2 \cdot m_{polymer}}{1 - x\ SiO_2} \quad (1)$$

$$n_{GPTMS} = \frac{m_{SiO_2}}{MSiO_2} \quad (2)$$

where $xSiO_2$ is the weight fraction of SiO_2 to be introduced into the polymeric matrix, m_{SiO2} is the mass of silica to be added, M_{SiO2} is the molecular weight of silica (60.08 g/mol), considering the complete condensation of GPTMS, and n_{GPTMS} is the number of moles of GPTMS precursor. The proportions used are summarized in Table 5.1. In order to facilitate the text reading, the membranes are referred as FucoPol+GPTMS and the percentage corresponding to the SiO_2.

Table 5.1: Hybrid polysaccharide membranes prepared using different concentrations of GPTMS SiO_2 precursor in the sol-gel method.

Membrane	GPTMS (µl)	Acetic acid (µl)
FucoPol+GPTMS 3	17.05	1.68
FucoPol+GPTMS 5	29.02	2.85
FucoPol+GPTMS 7	41.54	4.13
FucoPol+GPTMS 7.5	44.71	4.40
FucoPol+GPTMS 8.0	47.95	4.72

The hybrid membranes were prepared by dissolution of 1.5 w/v% of the dried FucoPol in distilled water during 8 h, at room temperature. Then, acetic acid glacial was added as acid catalyst, for obtaining acidic conditions (pH 3-4) during the sol reaction, in order to functionalise the biopolymer with the silica precursor of GPTMS [135]. After this, a calculated amount of GPTMS (see Table 5.1) in order to obtain hybrid membranes with a final SiO_2 content of 3.0, 5.0, 7.0, 7.5 and 8.0 w/w%, with respect to the biopolymer, was also added dropwise under vigorous magnetically stirring to the aqueous solution, to develop a good dispersion of the silica particles in the polymeric matrix. The film forming solution of hybrid polysaccharide membranes was maintained under stirring overnight at room temperature (22.0 ± 1.0 ºC). In order to degas the film forming solution and facilitate the dispersion of the inorganic content, it was sonicated during 25 min before casting the membranes in Teflon petri dishes. They were dried at 30.0 ºC in an oven during 72 h, for completing dehydration and condensation reaction of SiO_2 and promoting linkages with FucoPol chains.

The membranes prepared with optimized molar ratios were immersed for crosslinking reaction with a solution of calcium chloride (2 g/100 ml) during 5 min. The excess liquid was removed using a tissue paper and the membranes were dried at ambient temperature and relative humidity (T=22.0 ºC and RH=48%).

5.3.3 Characterisation of the hybrid polysaccharide membranes

5.3.3.1 Fourier transform infrared (FT-IR) spectroscopy

Fourier Transform Infrared Spectra (FT-IR) of the hybrid polysaccharide membranes were recorded using attenuated total reflectance (ATR) on a Bruker Spectrometer IFS 66/S FT-IR instrument (USA), equipped by H-ATR with a ZnSe crystal. The chemical structure of the membranes was checked by analysing normalized spectra obtained in the range of wave numbers from 4000 to 550 cm^{-1} during 120 scans, with 2 cm^{-1} resolution. The analysis was

performed with the membranes without calcium chloride and after crosslinking with calcium chloride solution, in order to understand the effect of calcium chloride in their structure. Finally, they were also compared with the results obtained for FucoPol.

5.3.3.2 Thermogravimetry analysis (TGA)

The thermal stability of the hybrid polysaccharide membranes developed and pristine FucoPol was studied by thermogravimetric analysis using a TA TGA Q-50 analyser (TA Instruments, USA). The TGA curves were obtained with a ramp of 10.0 ºC/min under a nitrogen flow of 40 ml/min, using approximately 7.0 mg of sample placed into an aluminium sample pan. The thermal stability and inorganic content of samples were calculated from analysed curves from 25 to 600 ºC [146].

5.3.3.3 Differential scanning calorimetry (DSC)

DSC analysis were performed on a TA DSC Q-200 equipment (TA Instruments, USA), using approximately 5.0 mg of each sample, in order to determine the glass transition temperature of FucoPol and hybrid polysaccharide membranes prepared by the sol-gel process. The samples were previously dried in a desiccator and placed into an aluminium sample pan. The analysis was carried out in a nitrogen atmosphere with a flow rate of 40.0 ml/min and a heating rate of 10.0 ºC/min. The DSC thermograms were obtained in the range of 0‑130.0 ºC. This upper limit for DSC was selected in order to avoid the decomposition of polymers and membranes, as seen by TGA.

5.3.3.4 Morphological characterisation of composite membranes

The morphological characterisation was carried out by scanning electron microscopy (SEM) using a field emission scanning electron microscope (Jeol JSM7001F, Oxford).

5.3.3.5 Swelling and leaching analysis

The swelling and leaching were analysed upon immersion of the membranes, during 24h at 30.0 ºC, in water, ethanol and a solution of 10.0 wt.% of water in ethanol, in order to evaluate the affinity and stability of the membranes to these solvents.

The experiments were performed as following: (i) the membranes at room humidity and temperature (T=22.0 ºC and RH=48%) were weighed; (ii) then, they were immersed in the solvents for 24 hours; (iii) after this procedure, they were removed from the liquid, cleaned with tissue paper and weighed; (iv) at the end, the membranes were dried in an oven at 70.0 ºC during 24 h and weighed again. The ethanol used was previously dried with molecular sieves 4 Å (Sigma-

Aldrich, USA), before the swelling and leaching experiments, and all samples of membranes were weighed using a digital balance (Kern ABJ 220-4NM, Germany). On the other hand, in order to account the water present in the membrane (m_{H2O}), a sample of the same membrane used for the swelling and leaching experiments was dried in the oven at 70.0 ºC during 24 h. m_{H2O} was calculated by the difference between the weight of dried membrane (after drying at 70 ºC) and m_1 (weight of the membrane at room humidity and temperature).

Swelling and leaching were calculated using equations 3 and 4, respectively:

$$Swelling\ (wt\%) = \frac{(m_2 - (m_3 - m_{H_2O}))}{m_1} \times 100 \quad (3)$$

$$Leaching\ (wt\%) = \frac{(m_3 - (m_1 + m_{H_2O}))}{m_1} \times 100 \quad (4)$$

where m_1 is the weight of the membrane at room humidity and temperature (48.0% RH and 22.0 ºC) and m_2 and m_3 are the weights of the swollen and dried membranes (at 70.0 ºC), respectively.

5.3.3.6 Mechanical properties

The mechanical properties, tensile strength and elongation at break, were measured using a TA-Xtplus texture analyser (Stable Micro Systems, Surrey, England) at 48.0% RH and 22.0 ºC. The membranes were fixed with tensile grips and stretched at a rate of 0.5 mm/s in a tension mode. These experiments were conducted at least three times.

5.3.3.7 Biodegradability tests

The biodegradability tests of the membranes prepared were carried out according to Alves *et al.* (2011) [97]. A volume of 50.0 ml of nutrient medium (composed by 10 g/l of tryptone, 5 g/l of yeast extract and 10 g/l of sodium chloride) were mixed with 10 g of soil. Thereafter, the suspension was decanted, filtered and incubated at 30.0 ºC for 24 h. The hybrid polysaccharide membranes (2 cm x 2 cm) were placed in a Petri dish with a culture medium supported in a nutrient medium of agar and inoculated with the prepared microbial culture. The membrane samples were placed during 90 days, in a room (with controlled adjustment of the atmospheric conditions of 46.0-50.0 %RH and 18.0-30.0 ºC of temperature). Besides the hybrid polysaccharide membrane developed,

two more samples were employed as positive and negative case studies of biodegradability: a carboxymethylcellulose (CMC) sodium pristine film (the salt dissolved in water) was used as a positive, and a non-biodegradable polymer low density, polyethylene (LDPE), was used as a negative.

On the other hand, at the same time, another study of biodegradability was performed in the same conditions as described above, in order to quantify the weight loss of the membranes over time. This study was based on the work of Wu et al. (2017) [147]. Hybrid polysaccharide membrane samples were buried at 3-5 cm depth in pots containing soil. A control pot with the non-biodegradable polymer (LDPE) and a biodegradable film (CMC) were also quantified. Over time, the samples were retrieved from the soil, washed in distilled water and dried for 24 h in an oven at 40.0 ºC. During the same period that the membranes were out of the pots, the soil was watered with 30 ml of water. Then the samples were weighed before returning to soil.

5.3.4 Transport performance and stability of the hybrid membranes for ethanol dehydration

The transport performance of the hybrid membranes was tested for ethanol dehydration by pervaporation. The experimental set-up used is described in Fig. 5.1.

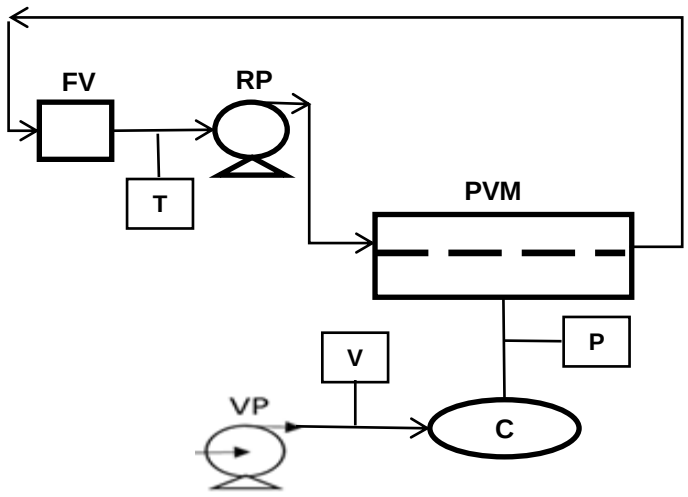


Fig. 5.1: Schematic diagram of pervaporation system. FV: feed vessel; RP: recirculation pump (Lead Fluid BT/101S, China); PVM: pervaporation module; VP: vacuum pump (PFEIFFER Duo 2.5; Germany); C: condenser; V: valve; P: pressure transducer; T: temperature controller.

Experiments were carried out at constant temperature of 30.1 ± 0.4 ºC, using 10.0 wt.% of water in ethanol. The effective surface area of the membrane was 7.54 cm^2 and the pervaporation driving force was maintained at a pressure of 1.0 ± 0.1 mbar in the downstream circuit. Each

experiment lasted at least 3 h, after preconditioning the membrane for 30 min with the feed solution. The concentrations of ethanol in the feed solution and permeate were measured by refractive index using an Abbe 5 refractometer (Bellingham + Stanley, USA).

The transport properties of the membranes were quantified in terms of water and ethanol permeabilities and selectivity, in order to understand the intrinsic performance of the membranes under different experimental conditions.

In order to evaluate the stability of the hybrid polysaccharide membranes in a real situation, the membranes were kept in contact with a solution of 10.0 wt.% of water in ethanol, at 30.0 ºC, during 7 days, and consecutive pervaporation experiments were performed during this period.

5.3.5 Transport performance and stability of the membranes for gas dehydration

These experiments were carried out to understand the possibility of using these hybrid polysaccharide membranes in gas dehydration.

The experiments were performed in the membrane cell used for pervaporation, under vacuum (approximately 70 mbar of absolute pressure). However, in this case, the feed was nitrogen with a relative humidity of 52.0 % (achieved by circulating the gas through a saturated solution of magnesium nitrate hexahydrate). Three experiments in three consecutive days were run during 6 h each (in a total of 18 h of permeation). The membrane was dried with helium before and after each experiment. The permeate was analysed by on-line mass spectrometry as described in Fraga *et al.* (2018) [148].

5.4 Results and discussion

5.4.1 Selection of hybrid membrane composition

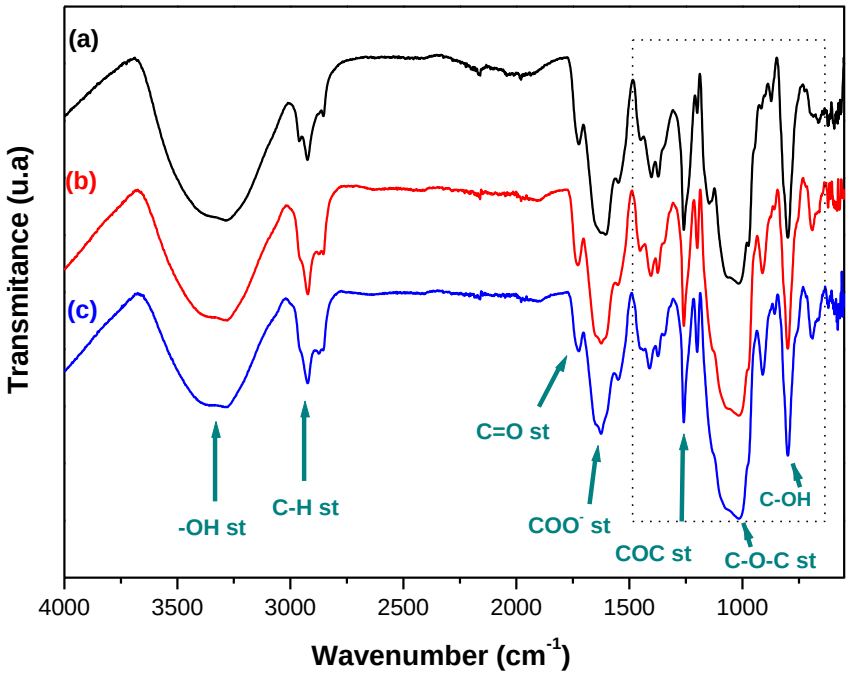
Each membrane prepared was immersed in distilled water during 24 h, in order to test their water resistance and membrane properties after contact with water. The membranes with 3.0 and 5.0 wt.% of silica precursor did not exhibited enough mechanical strength for permeation experiments, since they become brittle after being in contact with water. Additionally, the membranes with 7.5 and 8.0 wt.% of silica precursor exhibited fractures after drying, indicating incompatibility between the silica precursor and the polysaccharide matrix. On the other hand, the membrane with 7.0 wt.% of silica precursor, FucoPol+GPTMS 7 membrane, was homogeneous, resistant to water and mechanically stable. Thus, for characterisation and permeation experiments only this optimized membrane was considered.

5.4.2 Characterisation of the hybrid polysaccharide membranes

5.4.2.1 FT-IR results

The FT-IR spectra of the hybrid polysaccharide membranes and FucoPol are depicted in Fig. 5.2.

i)



ii)

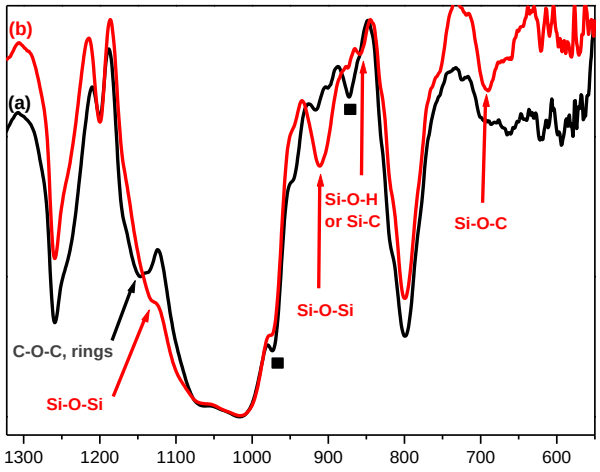


Fig. 5.2: i) FT-IR spectra of: a) pristine FucoPol; b) FucoPol+GPTMS 7 hybrid membrane and c) FucoPol+GPTMS 7+$CaCl_2$ hybrid membrane; ii) amplification of part of spectra of a) pristine FucoPol and b) FucoPol+GPTMS 7 hybrid membrane.

The spectra of the modified membranes and FucoPol are comparable and show the characteristic bands common to all polysaccharides portraying carboxylic acids (Fig. 5.2): around 3300 cm^{-1} it can be observed the band that corresponds to the O-H stretching of hydroxyls, carboxylic acids and bound water; at around 2900 cm^{-1} there is a band that corresponds to the aliphatic C-H stretching vibration of CH_2 groups; the band noticeable at around 1720 cm^{-1} corresponds to the stretching vibration of C=O of carbonyls in carboxylic groups and the bands at 1625 cm^{-1} and 1407 cm^{-1} can be attributed to the asymmetric and symmetric stretching of carboxylates [149], respectively. These results are in accordance with the findings reported by Freitas *et al.* (2011) [2], that also characterised FucoPol. The band around 1259 cm^{-1} is associated to vibrations assigned to C-O-C bonds of acetyl esters [150] and around 1200 cm^{-1} corresponds to the deformation of the O-H bond [149]. Finally, the band at 1148 cm^{-1} corresponds to the stretching vibration of glycosidic bonds [150], the bands present at 1010 cm^{-1} and 800 cm^{-1} correspond to the asymmetric stretching vibration of for C-O-C bonds [149] and to the skeletal vibration of C-OH bonds in the rings [150], respectively.

After modification with the GPTMS precursor, a new band around 2875 cm^{-1} associated with the C-H strength of GPTMS crosslinking appeared. Moreover, the intensity of the band corresponding to O-H bonds around 3300 cm^{-1} decreased. This means that the first modification of GPTMS occurred through the attachment to hydroxyl groups present in Fucopol [151,152]. The typical wide band of Si-O bond appeared at around 1130 cm^{-1} and around 1110 cm^{-1} for FucoPol, while a new band emerged at around 910 cm^{-1} for the modified hybrid membranes (Fucopol+GPTMS 7 and FucoPol+GPTMS 7+$CaCl_2$), presumably associated to the Si-O-Si bond [153]. These results indicate that GPTMS has been successfully grafted onto the polymer and also that the SiO_2 network was created. Furthermore, the presence of new peaks at 857 cm^{-1} associated with Si-O-H groups and Si-C bond [149], and a band at 690 cm^{-1}, corresponding to Si-O-C bonds [154], demonstrates that the sylanization reaction could be also preceded by attachment of silanols groups to the hydroxyl groups of the FucoPol backbone [152].

On the other hand, the crosslinking reaction with Ca^{2+} did not change the main polymer structure, when comparing with the hybrid polysaccharide membrane FucoPol+GPTMS 7. However, as expected, the interaction of Ca^{2+} with the polar –OH groups decreases the intensity of the band around 3300 cm^{-1} (see Fig. 5.2). Bands 1728 cm^{-1} and 1625 cm^{-1} are associated, respectively, to the stretching vibration of carboxylic groups and asymmetric stretching of carboxylates, whereas the band at 1453 cm^{-1} in FucoPol+GPTMS 7 becomes wider in the FucoPol+GPTMS 7+$CaCl_2$ membrane, indicating that the presence of Ca^{2+} ions changed the environmental of the chains, affecting the conformational properties of the polymeric structure [155].

5.4.2.2 TGA analysis

The FucoPol and hybrid polysaccharide membranes prepared – FucoPol+GPTMS 7 and FucoPol+GPTMS 7+$CaCl_2$ – exhibited a thermal degradation in three stages (Fig. 5.3 and Table

5.2). All graphs exhibited a first step of degradation with a Td (onset) of 31 ºC, 35 ºC and 40 ºC for FucoPol, FucoPol+GPTMS 7 and Fucopol+GPTMS 7+$CaCl_2$ membranes, respectively, corresponding to the removal of physically adsorbed water. However, the weight loss in this first stage of membranes decomposition were 14 %, 13 % and 10 %, respectively for FucoPol, FucoPol+GPTMS 7 and FucoPol+GPTMS 7+$CaCl_2$, probable due to the loss of polar groups available to interact with water after bonding to Ca^{2+} ions. These results also suggest that the hybrid membranes physically adsorbed water more strongly than FucoPol, as a consequence of the presence of the SiO_2 network, in accordance with the results reported by Choudhari *et al.* (2016) [141]. They found that hybrid membranes of alginate have a higher decrease in weight loss in the first stage, compared with the pristine alginate membrane. Furthermore, the lower temperatures for pure FucoPol indicate the removal of water in free form or weakly adsorbed onto the surface.

The second step, in the range of 230-251 ºC (see Table 5.2), was attributed to the cleavage of polymer lateral chains and decomposition of the polymer network connected with water through hydrogen bonding. The third stage, between 339 and 379 ºC, could be considered as the weight loss referred to the structure collapse of the polymer and thermal decomposition of sugar cyclic residues.

As expected, the residue obtained at 600 ºC (Fig. 5.3) increased with the presence of SiO_2 and calcium, compared with the FucoPol residue (20 %, corresponding to salts not removed during the purification of the polysaccharide). In the case of the hybrid membranes, without and with $CaCl_2$, the residues obtained represent 26 % and 34 %, respectively. This corresponds to 6 wt.% in SiO_2, in accordance with the amount calculated using equations 1 and 2. In the case of FucoPol+GPTMS 7+$CaCl_2$, the additional 8 wt.% in inorganic content can be associated to a probable formation of $CaCO_3$ during thermal degradation.

Table 5.2: TGA results of FucoPol and the hybrid polysaccharide membranes prepared.

Sample	Td $_{onset}$ (1st step) (ºC)	Td $_{onset}$ (2nd step) (ºC)	Td $_{onset}$ (3rd step) (ºC)	Residue (%) (600 ºC)
FucoPol	31	230	378	20
FucoPol+GPTMS 7	35	240	339	26
FucoPol+GPTMS 7+$CaCl_2$	40	251	369	34

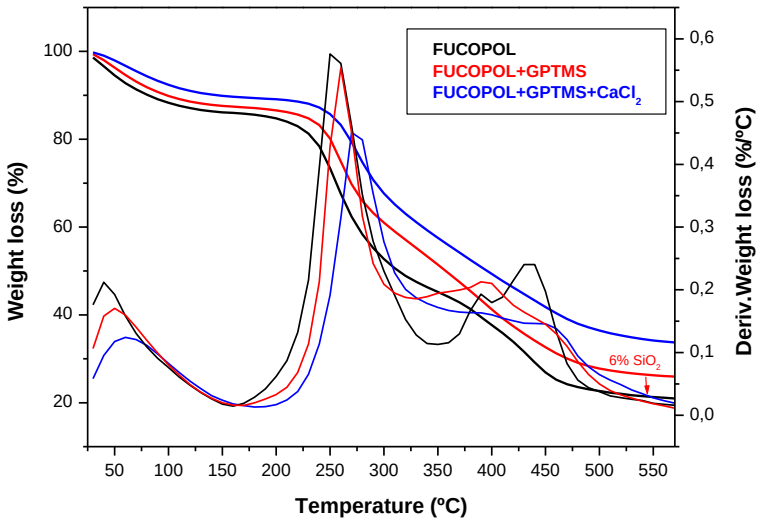


Fig. 5.3: Thermograms of TGA analysis of FucoPol and hybrid polysaccharide membranes (FucoPol+GPTMS 7 and FucoPol+GPTMS 7+$CaCl_2$).

5.4.2.3 DSC results

The results of the DSC analysis are presented in Fig. 5.4.

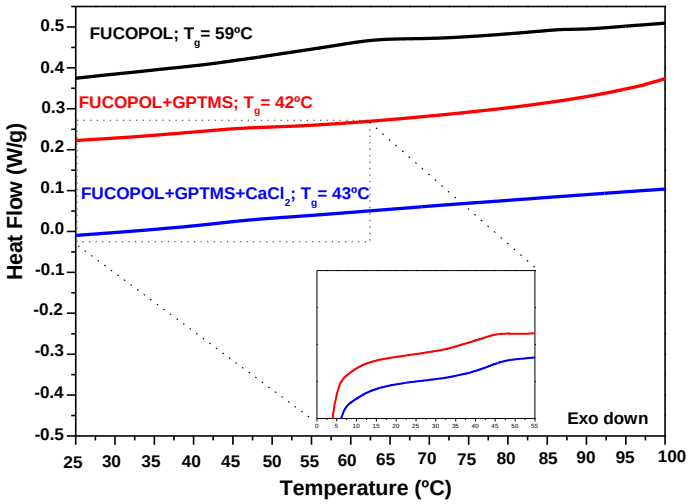


Fig. 5.4: DSC results for the FucoPol and hybrid polysaccharide membranes, with and without calcium chloride crosslinking - FucoPol+GPTMS7+$CaCl_2$ and FucoPol+GPTMS 7, respectively.

The DSC thermograms for heating runs (first heating scan) of crosslinked hybrid polysaccharide membranes exhibited a unique glass transition temperature confirming that there was no phase segregation between inorganic and organic phase during modification. The FucoPol glass temperature (Tg) was 59 ºC, while for FucoPol+GPTMS 7 and FucoPol+GPTMS 7+ $CaCl_2$ was 42 and 43 ºC, respectively. This decrease of glass transition temperature in the case of the hybrid membranes indicates a lower rigidity compared with FucoPol, which is in accordance with data reported in the literature for other polymers crosslinked with the GPTMS precursor [156]. The decrease of Tg in the hybrid polysaccharide membranes could be firstly attributed to the percentage reduction of the intermolecular attraction forces of hydrogen bonds between carboxylic groups and –OH groups (in accordance with that observed by FT-IR – see section 5.4.2.1) and, secondly, due to the disruption of the SiO_2 network which avoids the interaction between hydrogen bonds and the carboxylic hydroxyl groups. Moreover, as described in the TGA analysis (see section 5.4.2.2), the presence of more water adsorbed in the hybrid polysaccharide membranes can act as a plasticizer reducing the rigidity of the polymer backbone and avoiding the loss of hydrogen bond interactions between carboxylic groups.

5.4.2.4 Morphological structure of the hybrid membranes

The images of the SEM analysis (Fig. 5.5) show that the hybrid polysaccharide membranes have a dense surface without defects. The cross-section image (Fig. 5.5 b)) presents the same reorganization between the polysaccharide chains and the silica precursor over all biopolymer matrix.

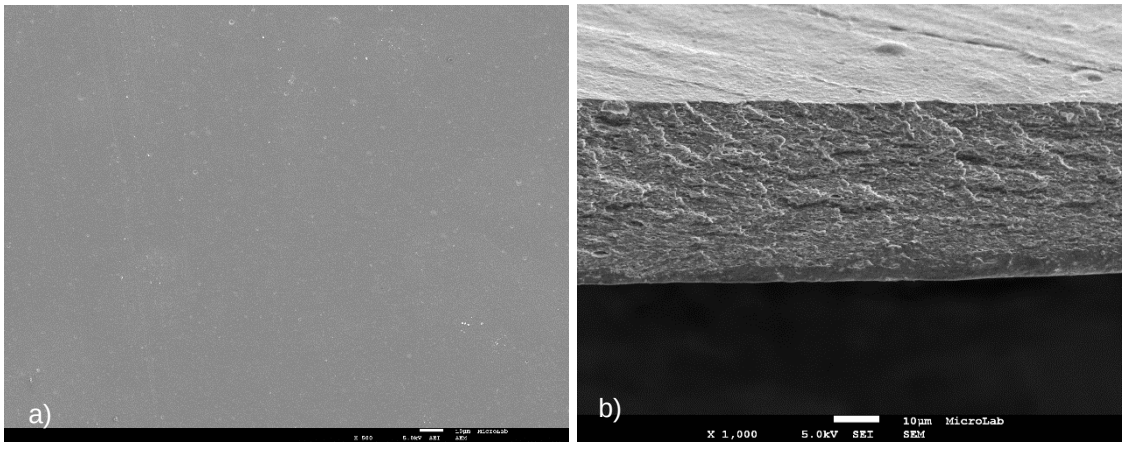


Fig. 5.5: SEM images of the hybrid polysaccharide membrane: a) surface and b) cross-section.

5.4.2.5 Swelling and leaching results

The hybrid polysaccharide membrane (FucoPol+GPTMS 7+$CaCl_2$) presents a value of swelling (Table 5.3) of 47.5 wt.% in the presence of water, which means that the crosslinking reactions

between the polysaccharide and the silica precursor and, the dried hybrid membrane with calcium chloride, turns the membrane less prone to water solubilisation and retention. However, this membrane keeps its affinity for water in comparison with ethanol.

Table 5.3: Swelling and leaching of the FucoPol+GPTMS 7+$CaCl_2$ membranes.

Solvent	Swelling (wt.%)	Leaching (wt.%)
Water	47.5 ± 2.2	-4.3 ± 0.2
Ethanol	8.8 ± 2.3	5.3 ± 0.3
10.0 wt.% water/ethanol	14.8 ± 1.7	4.0 ± 1.4

The leaching values obtained are relatively low. In the case of pure water, the leaching value is negative, which means that the hybrid membrane is leached more significantly in the presence of water, losing components that solubilise. This membrane swells in the presence of water and the solubilised water facilitates the solubilisation of material not so strongly linked to the polymer backbone, originating a leaching effect. A strong leaching is an indicator of potential problems of stability under operating conditions, when the membrane has to face for a prolonged period of time the presence of water as solvent medium. In the presence of ethanol, the leaching effect is not so significant.

5.4.2.6 Mechanical properties

In order to study the effect of crosslinking (by immersion with $CaCl_2$) in the stability of the membrane, two membranes were analysed – FucoPol made by the sol-gel process using a GPTMS precursor (FucoPol+GPTMS 7); and FucoPol with GPTMS and crosslinked with calcium chloride (FucoPol+GPTMS 7+$CaCl_2$). The results obtained are shown in Table 5.4.

Table 5.4: Mechanical properties of the hybrid polysaccharide membrane before crosslinking with $CaCl_2$ (FucoPol+GPTMS 7) and after crosslinking (FucoPol+GPTMS 7+$CaCl_2$).

Membrane	Tensile strength (MPa)	Elongation at break (%)	Young modulus (MPa)
FucoPol+GPTMS 7	26.2 ± 10.4	6.6 ± 0.5	405.9 ± 148.2
FucoPol+GPTMS 7+$CaCl_2$	26.1 ± 5.9	10.4 ± 2.5	424.2 ± .83.4

Hybrid polysaccharide membranes without and with $CaCl_2$ present similar results of stress at break (26.2 MPa and 26.1 MPa) and Young's Modulus, which demonstrates that the crosslinking by immersion with $CaCl_2$ does not affect the resistance of the membranes to deformation. On the other hand, the elongation at break of the FucoPol+GPTMS 7+$CaCl_2$ membrane is slightly higher than the elongation at break of the FucoPol+GPTMS 7 membrane without the crosslinking with calcium chloride, but the differences are not significant, since the values fall within the error. From these results, we can conclude that the hybrid polysaccharide membranes present a similar stability to deformation with or without $CaCl_2$.

In a previous study, Meireles *et al.* [144] prepared membranes of FucoPol using genipin as crosslinking agent. Comparing the results of the mechanical properties of the membranes with genipin and the hybrid membranes prepared in this work, it can be noticed that the hybrid membranes have a higher Young's modulus (424.2 MPa and 155.6 MPa, respectively), higher tensile strength (26.1 MPa and 3.1 MPa) and higher elongation at break (10.4 % and 2.8 %) under the same conditions. These results indicate that the hybrid membranes present a higher resistance to deformation and are more elastic than the membranes prepared with genipin, which represents an improvement of the mechanical properties.

5.4.2.7 Biodegradability results

The evaluation of biodegradability was carried out through two distinct analyses, as previously described: 1 - samples were placed in agar Petri dishes containing a rich nutrient medium; 2 - buried in soil. As control, a CMC biodegradable membrane and LDPE non-biodegradable membrane were used.

From the results of the biodegradability measurement in Petri dishes, we concluded that the CMC film (presented as control of a biodegradable membrane), was highly degraded (observed within 7 days). Contrarily, the LDPE film remained unchanged throughout the experiment. The hybrid polysaccharide membrane seems to have an increase in size and some biological activity on the membrane was noticed. Comparing the results reported by Alves *et al.* (2011) [97] for GalactoPol (an exopolysaccharide produced by *Pseudomonas oleovorans*), FucoPol+GPTMS 7+CaCl2 presents a much lower degradability. After 8 days, microbial growth could be observed covering the surface of the GalactoPol membrane; this result was only slightly observed for the FucoPol hybrid membrane.

In Fig. 5.6 the weight loss for the membranes used are shown with exception of the CMC membrane, because at the end of the first week this membrane could no longer be distinguished from the soil.

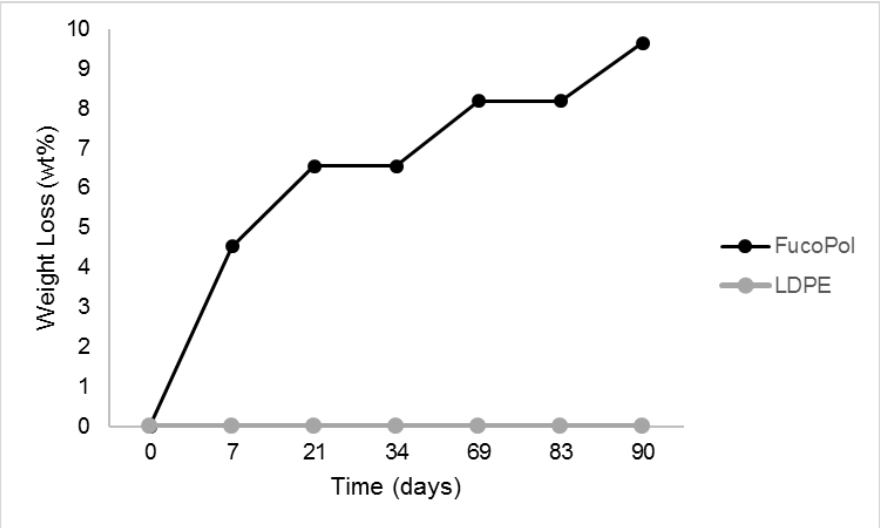


Fig. 5.6: Weight loss of the hybrid polysaccharide membranes (FucoPol) and LDPE film as a function of incubation time in soil.

Fig. 5.6 shows that the hybrid polysaccharide membrane was slowly degraded over time, with a 10 wt.% degradation after 90 days. On the other hand, it was noticed a constant weight during some periods (periods between 21 and 34 days and between 69 and 83 days), which correspond to the periods of time where the temperature was around 18.0 ºC. During the periods where the temperature was above 18.0 ºC it was not observed a higher degradability of the membrane. This result means that the biodegradability rate varies according to the soil temperature, being the biological activity favoured at higher temperatures, which is in accordance with the study performed by Vieira & Nahas (2005) [157].

In conclusion, from the results obtained it can be concluded that the hybrid polysaccharide membrane does not present a fast biological degradability, which assures the required integrity for operation during long periods. On the other hand, the fact that this membrane, which comprises a biopolymer as backbone, is biodegradable in contact with soil is extremely positive in what concerns the impact of its disposal in the environment.

5.4.3 Transport performance and stability of the hybrid membranes for ethanol dehydration by pervaporation

The transport performance of the hybrid polysaccharide membranes was measured for ethanol dehydration with 10.0 wt.% of water. Results of FucoPol+GPTMS 7+$CaCl_2$ transport performance are presented in Table 5.5.

As described in our previous work ([158]), in order to do a better quantification of the transport performance of the membranes and, moreover, compare these results with others referred in the

literature, the permeability and selectivity of the membrane were calculated using the solution-diffusion model (equation 5). In this way, the contribution of the membrane to the transport behaviour can be explained and quantified, without the interference of operating conditions [70].

$$J_i = \frac{P_i}{\delta}(p_{i,feed} - p_{i,perm}) \Leftrightarrow J_i = \frac{P_i}{\delta}(\gamma_{i,feed}\, x_{i,feed}\, p_{i,feed}^{sat} - p_{i,perm}) \quad (5)$$

where i is the target compound (water or ethanol), J_i is the molar flux of that particular compound (mol/m^2.s), P_i is the permeability (mol/m.s.Pa), p_i is the partial pressure (Pa), δ is the thickness of dense active layer of the composite membrane (m), γ_i is the activity coefficient of the target compound (-), x_i is its molar fraction in the feed stream (-) and p_i^{sat} is the saturation vapor pressure (Pa).

The permeability values were obtained using equation 5 and the selectivity was calculated as the ratio between the permeability of water and permeability of ethanol.

Table 5.5: Transport performance of FucoPol+GPTMS 7+$CaCl_2$ developed by the sol-gel process (T=30.0 ºC; downstream pressure = 1.0 mbar).

P_w x 10^{12} (mol/m.s.Pa)	**P_{et} x10^{13} (mol/m.s.Pa)**	**Selectivity (w-et)**
6.6 ± 0.4	0.1(2) ± 0.0(2)	566 ± 49

The total mass flux of this membrane is approximately 14.2 g/m^2.h, however, this flux is composed mainly by water (almost 50 x higher than the flux of ethanol), which indicates that the hybrid polysaccharide membrane has a much higher selectivity for water than for ethanol.

The results shown in Table 5.5 allow to conclude that the hybrid polysaccharide membrane presents a much higher affinity for water than for ethanol (in line with the results obtained during the swelling studies – see section 5.4.2.5). This membrane shows a much higher permeability for water, which results in a high selectivity value.

Table 5.6: Comparison of the transport performance of FucoPol+GPTMS 7+$CaCl_2$ with other membranes, referred in literature for ethanol dehydration.

Membrane	$[Water]_{feed}$ (wt.%)	T (ºC)	δ active layer (µm)	P_w x 10^{12} (mol/m.s.Pa)	P_{et} x10^{13} (mol/m.s.Pa)	Selectivity (w-et)	Reference
FucoPol+GPTMS 7+$CaCl_2$	10.2	30	~61.1	6.6	0.12	566	Present work
GalactoPol-PES[a]	10.4	30	12.5	3.8	0.29	134	Meireles *et al.* (2013) [158]
PERVAP® 4101	9.9	30	~3.5	7.2	0.13	554	Meireles *et al.* (2013) [158]
FucoPol+Genipin-PES	10.2	30	21.1	11.9	0.83	143	Meireles *et al.* (2015) [144]
CS-Ti-DHPPA/PAN[b]	10.0	30	0.25	0.1(8)	0.00(7)	270	Zhao *et al.* (2013) [127]
AlgCa+Fe_3O_4[c]	3.0	23	28	-	-	48	Dudek *et al.* (2017) [124]

[a]GalactoPol-PES – composite membrane of exopolysaccharide composed by galactose and produced by *Pseudomonas oleovorans*; and polyethersulfone (PES) as support; [b]CS-Ti-DHPPA/PAN – chitosan incorporated with a $TiCl_4$ using as modifier 3-(3,4-Dihydroxyphenyl)propionic acid (DHPPA), and polyacrylonitrile as support of composite membrane; [c]AlgCa+Fe_3O_4 – alginate crosslinking with ions of Ca^{2+} and incorporated with ferroferric oxides

Comparing the FucoPol+GPTMS 7+$CaCl_2$ with other membranes referred in literature (Table 5.6), it can be observed that the membrane developed in this study presents the lowest ethanol permeability, with exception of the hybrid membrane developed by Zhao *et al.* (2013). Also, the FucoPol hybrid membrane presents higher selectivity when compared with other hybrid biopolymer membranes referred, meaning that this membrane exhibits better transport performance than other biopolymer membranes.

Both composite membranes, developed in our previous works ([144,158] present similar results of water and ethanol permeability and selectivity, although lower than PERVAP® 4101 (commercial membrane composed by poly(vinyl alcohol) PVA), which shows a higher water permeability and selectivity. However, the FucoPol hybrid membrane shows a very good

performance with values of permeability and selectivity very close to the ones exhibited by the commercial membrane.

As the FucoPol hybrid membrane showed such a promising transport performance, slightly higher than the commercial membrane PERVAP® produced from Sulzer, it was necessary to assess the operating stability of this membrane under long-term operation and repeated use [127,159]. The results obtained for consecutive pervaporation experiments performed during 7 days, with repeated use of the hybrid polysaccharide membrane, are shown in Table 5.7.

Table 5.7: Stability of the hybrid polysaccharide membrane in three pervaporation consecutive experiments (using wet membranes in a solution of 10 wt.% of ethanol in water, with a total of 130 h). T=30 ºC and downstream pressure 1.0 mbar.

Experiment	P_w x 10^{12} (mol/m.s.Pa)	P_{et} x10^{13} (mol/m.s.Pa)	Selectivity (w-et)
1 (3 h)	7.7 ± 1.1	0.1(4) ± 0.0(2)	570 ± 117
2 (7 h)	9.7 ± 1.4	0.5(3) ± 0.0(8)	182 ± 37
3 (130 h)	14.7 ± 2.1	6.2 ± 0.9	24 ± 5

From these results it is clear that the hybrid polysaccharide membrane is not stable during repeated use. After 7 h, the membrane selectivity decreases drastically (from 570 to 182) and, after that, the membrane continues losing selectivity. This behaviour can be explained by the irreversible and excessive swelling of the membrane, creating a higher free volume between the polymer chains allowing water and ethanol molecules to diffuse more freely (the ethanol permeability increases from 0.14 to 6.20 x 10^{-13} mol/m.s.Pa). Also, the previously observed leaching (section 5.4.2.5) of material from the membrane to the surrounding feed solution may be related with the loss of compounds relevant for keeping the membrane structure (e.g. crosslinker). Under these circumstances, it was concluded that this membrane could not be used for direct contact with solvents containing such a high content in water.

5.4.4 Transport performance and stability of the membranes for gas dehydration

In order to perceive if the instability of the hybrid polysaccharide membranes was due to contact with the feed solution (ethanol and water), long-term operation experiments of gas dehydration were performed using nitrogen with a relative humidity of 52.0 %. The results obtained are shown in Table 5.8.

Table 5.8: Results of nitrogen dehydration by vapour permeation over time (absolute downstream pressure of ~70mbar, RH=52%, and $t_{experiment}$=6h each during three consecutive experiments).

Experiment	P_w (barrer*)	P_{N_2} (barrer)	Selectivity (w-N_2)
1	1953 ± 159	2.8 ± 1.1	703 ± 110
2	1987 ± 119	2.1 ± 1.2	961 ± 307
3	1958 ± 167	2.0 ± 0.2	959 ± 134

*The permeability in gases is expressed in barrer, where 1 barrer is 1 x 10^{-10} cm^3 (STP) cm/cm^2.s.cmHg =3.34 x 10^{-16} mol/m s Pa.

From Table 5.8 it is possible to infer that the hybrid polysaccharide membrane maintains the structural stability after being in contact with water vapour. Furthermore, from these preliminary results the membrane seems to be a good barrier for nitrogen, with permeability values extremely low (2.0 barrer), which is characteristic of polysaccharides [160]; and with a very high water permeability (almost 2000 barrer). Therefore, we may assume that these hybrid membranes are extremely promising candidates to perform gas dehydration.

5.5 Conclusions

This work evaluates new membrane materials obtained from a renewable source, for ethanol and gas dehydration. The novel hybrid polysaccharide membranes were prepared with FucoPol - produced by *Enterobacter* A47, using as carbon source the glycerol by-product of the biodiesel industry - and GPTMS as precursor of sol-gel reaction.

The hybrid FucoPol membranes developed showed high affinity towards water and adequate mechanical and thermal properties. These membranes were applied in ethanol dehydration, although irreversible swelling in the presence of water was noticed, compromising long term operation.

These hybrid membranes exhibited high selectivity to water vapor and showed a good stability during N_2/H_2O separation, constituting potential candidates for other industrial gas dehydration processes, such as biogas and flue gas.

Chapter 6

6 Evaluation of Hybrid Polysaccharide Membranes for Gas Dehydration using On-line Mass Spectrometry

Submitted as: Inês T. Meireles, Sofia C. Fraga, Rosa M. Huertas, Carla Brazinha, Isabel M. Coelhoso, João G. Crespo, Evaluation of hybrid polysaccharide membranes for gas dehydration using on-line mass spectrometry, Journal of Membrane Science (2018).

The membrane preparation for all the experiments presented here was developed by Rosa M. Huertas.The author was involved in all experiments, as well as, in the discussion and interpretation of the results, and preparation of manuscript. The experiments and elaboration of the data from mass spectrometry was performed in collaboration with Sofia C. Fraga.

6.1 Summary

The removal of water from gas streams, in particular flue gas and biogas, is an important industrial operation. To mimic these industrial dehydration processes, permeation of water vapour, pure gases (CO_2, CH_4 and N_2) and gas mixtures containing 20 vol.% CO_2 + 80 vol.% N_2 and 70 vol.% CH_4 + 30 vol.% CO_2, at different conditions of relative humidity, was monitored by mass spectrometry. The potential of using hybrid polysaccharide membranes obtained from a low cost carbon source (glycerol) and crosslinked using (3-Glycidyloxypropyl) trimethoxysilane (GPTMS) as silica precursor by a sol-gel method was evaluated. The hybrid membranes developed showed barrier properties to all gases studied, with a gas permeability below 1 barrer, while exhibiting high water permeabilities and selectivities. When process in a biogas mixture, the water permeability was found to be three times higher than water permeability in a flue gas mixture, leading to a H_2O/CH_4 selectivity much higher than H_2O/N_2 selectivity. These membranes showed, under close-to-real conditions, that they have the ability to dehydrate mixtures, with the advantage of not losing N_2 or CH_4, due to the low permeability values of these gases.

6.2 Introduction

Gas dehydration has a high industrial interest, since it can be used for the dehydration of natural gas, drying of compressed air, drying of gases for packaging purposes, roofing covers, humidity control in closed spaces, such as air conditioning in buildings, aviation and space flight, as well as water recovery from waste steam [18,38]. In particular, dehydration of flue gas, originated in the production of electricity by coal-fired power plants, has a great interest due to the energy

saving in power plants and reduction of diffusion of pollutants through water that can cause “gypsum rain” [36,161]. Other potential application is biogas dehydration which, after purification, can be used as an alternative to natural gas and be distributed as power supply in rural and urban areas [162,163].

When compared to other dehydration methods (e.g. adsorption using desiccants and condensation), membrane-based dehydration (or drying) of gaseous streams has numerous benefits [16]. Membrane technology may involve a lower energy consumption (since the only energy consumed is the one required to maintain a partial pressure difference across the membrane [16]) and smaller footprint. Additionally, this technology is usually rather flexible and involves a compact modular design, easy to maintain and control [41,42].

In gas dehydration, hydrophilic polymers, such as ethyl cellulose, cellulose acetate, polyacrylonitrile, sulfonated polyetheretherketone (SPEEK) and poly(vinyl alcohol) are usually used [38]. The –OH groups present in these type of polymers are able to interact with water molecules, which are incorporated and diffuse through the polymers [18,17,164]. In the present work, the potential of using hybrid polysaccharide membranes for gas dehydration is investigated. Hybrid polysaccharide membranes were prepared using a microbial exopolysaccharide rich in fucose (FucoPol) obtained from a low-cost, abundant carbon source: glycerol, produced as a by-product by the biodiesel industry. This biopolymer was purified using a solvent free method (dia-ultrafiltration), similarly to [165], in order to reduce the environmental impact and increase the membrane process sustainability. The hybrid membranes were prepared, as described in our previous work [166], by incorporation of a SiO_2 network homogeneously dispersed by a sol-gel method using (3-Glycidyloxypropyl) trimethoxysilane (GPTMS) as a crosslinker silica precursor, combining the best properties of the inorganic network with the selectivity of the microbial polysaccharides. Preliminary results [166] demonstrated that these membranes are able to selectively transport water vapour, are stable and have reproducible performance for nitrogen dehydration during extensive operation.

Understanding the water vapour interaction with the membrane is extremely important, since water has a high affinity to the polymer inducing swelling or plasticisation effects in the membrane structure [34,35]. The rearrangements caused by water vapour in the membrane structure impact on the membrane transport properties, namely in its flux and selectivity. On-line monitoring mass spectrometry (MS) has proved to be an efficient tool allowing to obtain the composition of the permeate stream at one data point each second (or less, if required), making possible to perform real-time monitoring during the whole permeation process. It has been used to characterise gas transport through dense membranes [34,35,167,168,148] as well as solute transport in pervaporation processes [168–171]. Moreover, mass spectrometry monitoring has the advantage of speed, smaller volume of samples, fewer losses of analytes and higher detection range, when compared to other techniques of detection, such as gas chromatography [169,172].

In this work, on-line mass spectrometry is used to monitor the permeation of water vapour and pure gases (CO_2, CH_4 and N_2) across the membranes developed, under different conditions of

relative humidity. Gas mixtures containing 20 vol.% CO_2 + 80 vol.% N_2 and 70 vol.% CH_4 + 30 vol.% CO_2 have also been studied to mimic industrial applications, namely flue gas and biogas dehydration [162,173].

6.3 Experimental

6.3.1 Materials

(3-Glycidyloxypropyl) trimethoxysilane (GPTMS) purchased from Sigma-Aldrich (USA) and acetic acid glacial (99-100%) purchased from J.T. Baker (USA), were used as precursor and acid catalyst, respectively, in the sol-gel process. Calcium chloride ($CaCl_2$) (>93.0 %) used as crosslinking agent was obtained from Fluka Analytical (USA); Magnesium nitrate hexahydrate (98.0 %) and magnesium chloride (99.0 %) were supplied by Alfa Aesar (UK), while sodium chloride (99.5 %) was purchased from Panreac Applichem (Spain). All these compounds were used to prepare the salt saturated solutions to adjust the water activity / relative humidity of the gases used in this work. Nitrogen (99.99 %), helium (99.99 %), carbon dioxide (99.99 %) and methane (99.99 %) used in the gas dehydration experiments were obtained from Irmasolda (Portugal).

6.3.2 Membrane preparation

The hybrid membranes were prepared as described in the previous work of Meireles *et al.* (2018) [166]. The pure dried biopolymer (1.5 %w/v) was diluted in distilled water during 8 h, at room temperature (20.0 ± 2.0 ºC). Then, 0.04 %v/v of acetic acid glacial was added as acid catalyst, and 7.0 w/w% of GPTMS precursor containing silica, was also added dropwise under vigorous magnetically stirring to the aqueous solution. The film forming solution for production of the hybrid polysaccharide membranes was maintained under stirring overnight at room temperature (around 22 ºC). After this, the aqueous solution was sonicated during 25 min, for degasification, before casting the membranes in Teflon petri dishes and drying at 30.0 ºC in an oven during 72 h. When the membranes were dried, a crosslinking reaction was accomplished by immersion of the membranes in a solution of calcium chloride (2 g/100 ml) during 5 min. The liquid in excess was removed using a tissue paper and the membranes were dried at an ambient temperature and relative humidity of 20.0 ± 2.0 ºC and 40.0 ± 3.0 %, respectively.

6.3.3 Single and mixed gas permeation experiments under dry and humidified conditions

The permeability of three different pure gases - CO_2, N_2 and CH_4 - was evaluated analysing the permeate composition by on-line mass spectrometry (MS) under vacuum conditions. The experimental set-up is represented in Fig. 6.1.

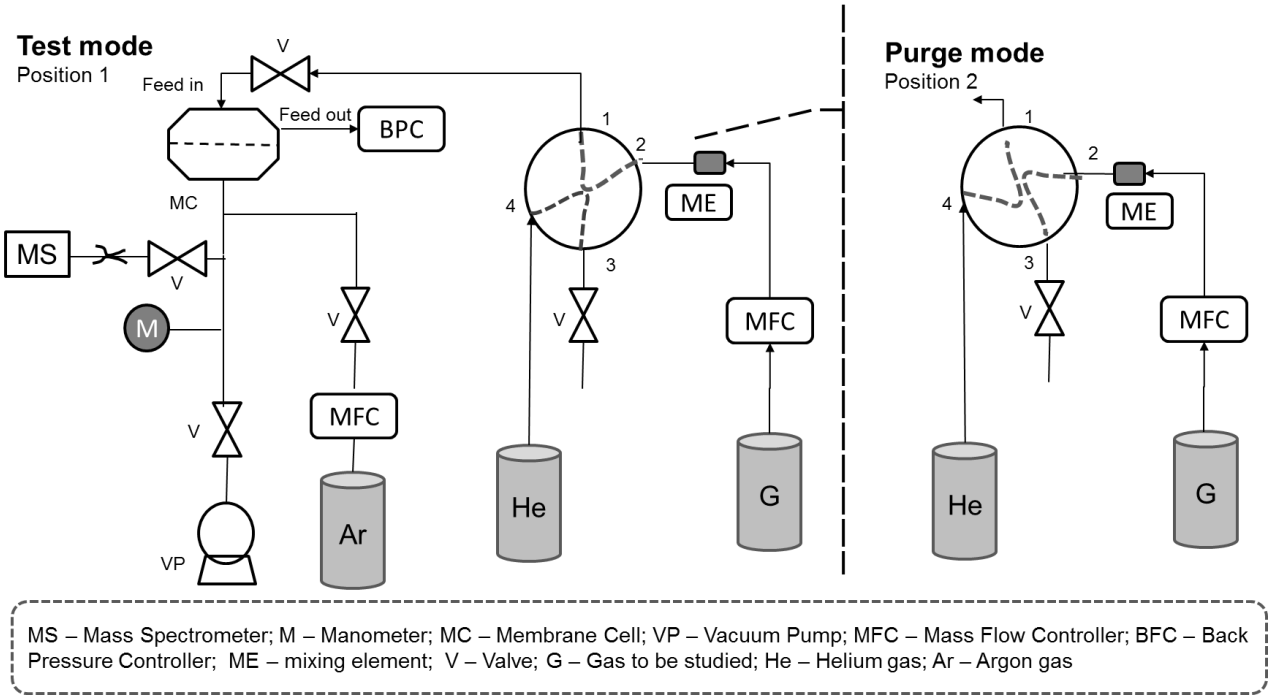


Fig. 6.1: Experimental set-up for pure dry gas permeation.

The experimental set-up consists in a membrane cell containing the membrane under study, mass flow controllers for each gas to be studied (EL-FLOW electronic, Bronkhorst, The Netherlands) and a back pressure controller (EL-PRESS electronic), in order to control the pressure of inlet and outlet streams of the membrane cell. A mass spectrometer (Prisma Plus QMG 220 M2, Pfeiffer Vacuum, Germany) with an axial beam ion source with an emission current of 1.0 mA and electron energy of 70.0 eV, single quadrupole and secondary electron multiplier SEM detection was used. The permeate side was maintained at low pressures through a dry, oil free diaphragm vacuum pump (Pfeiffer vacuum, MVP 015, Germany) and using a constant argon flux of 1.0 ml/min as an internal standard control fed directly to the permeate. The following operating parameters were controlled in all permeation experiments: feed pressure of gas at 1.05 bar, total flow rate of the inlet feed stream (pure gas) at 50.0 ml/min and argon flow rate of 1.0 ml/min. The temperature of the system was kept at 22.0 ± 2.0 ºC, to avoid variations in the signal of the MS during different permeation experiments. In order to clean the system and membrane, before and after each experiment, the feed side of the membrane cell is purged with helium. A four-way valve (as can be seen in Fig. 6.1) is used to switch from the purge mode (position 2) to the test mode

(position 1) in a fast way, without changing the inflow feed rate to the membrane cell. When the concentration of all gases under study in the permeate are at their lowest values (indicating that the system is completely clean), the gas stream under study is connected to the feed circuit using the four-way valve (test mode, position 1). After that, the permeate is monitored on-line with the MS for the composition of each gas (CO_2, N_2 and CH_4). The MS electrical signal is acquired and converted to volume fraction and partial pressure through the calibration method described in section 6.3.4. In this study, the following m/z signals were selected to detect the respective gases or vapours: m/z=4 for helium, m/z=18 for water vapour and m/z=40 for argon. For CO_2 we choose m/z=44 and 28, for N_2 m/z= 28 and 14 and for CH_4 m/z= 15 and 14, in order to increase the signal of these gases, taking into account that the experiments were performed under vacuum and the flux of gases through the membrane was low. In addition, it is necessary to assure which signals correspond to each gas when they are mixed, since some gases have overlapping signals (such as m/z=28, which corresponds to CO_2 and N_2).

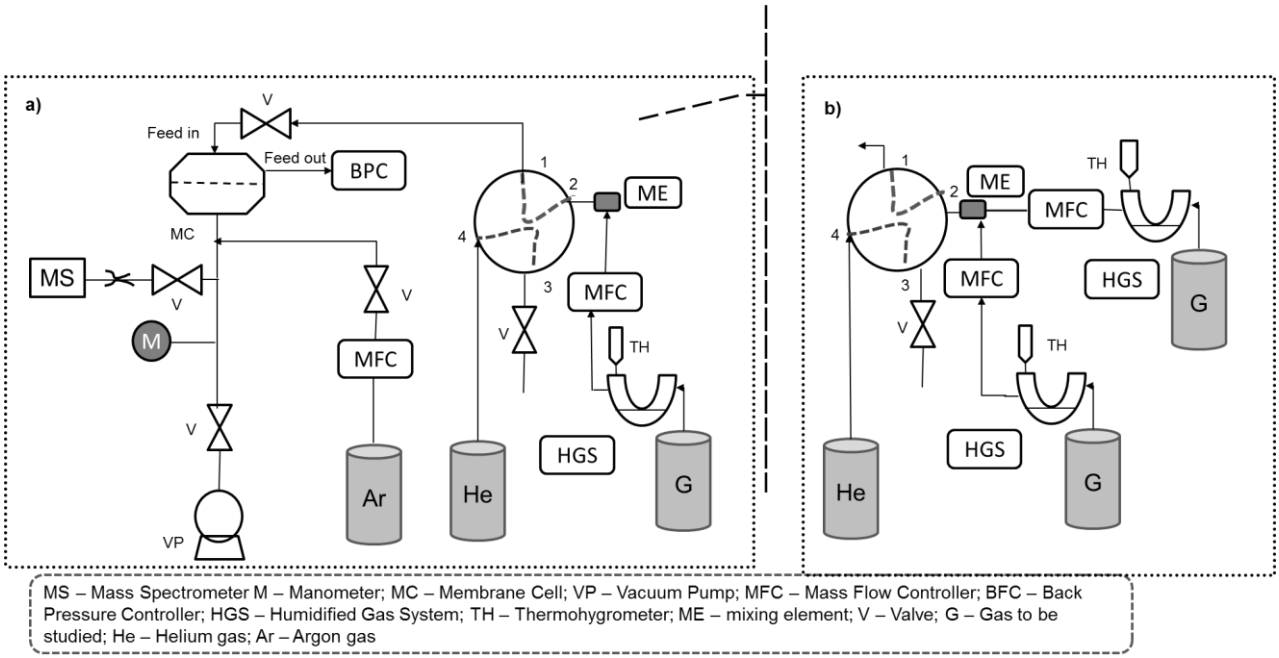


Fig. 6.2: Experimental set-up for permeation in test mode (position 1) of: a) humidified single gas and b) humidified mixture of gases.

When testing the permeation of humidified gases (see Fig. 6.2 a) and b)), each gas under study circulates through a trap that contains a saturated salt solution, with a defined water activity (referred in Fig. 6.2 as HGS – Humidified Gas System). Three different salt solutions were used, corresponding to different water activities (a_w) for the water-air system: magnesium chloride (a_w=0.324), magnesium nitrate (a_w=0.520) and sodium chloride (a_w=0.769). The water activity was calculated through equation 1:

$$a_w = \frac{p_w}{p_w^*} \qquad (1)$$

where p_w corresponds to the partial pressure of water in the feed and p_w* is the vapour saturation pressure of water calculated with the Antoine equation.

The temperature (ºC) and wt.% gas humidity content ($g_{H2O}/g_{dry\ gas}$), expressed as the percentage of the mass of water over the mass of dry gas/mixture of gas, were measured with a thermohygrometer (Vaisala HMI41 indicator and HMP42 probe, Finland). This humidity sensor uses as operating principle the changes on the capacitance of the sensor (thin polymer film) by absorbing water molecules [174]. The experiments were performed at least twice.

The experimental set-up shown in Fig. 6.2 b) was used to study the dehydration of flue gas and biogas. Before mixing, each gas circulates separately through the magnesium nitrate saturated solution (a_w=0.52 for the system water-air) and through the mass flow controller to assure a defined flow of each humidified gas and, consequently, a given mixture. After this, and before starting permeation, the humidified gas mixture is circulated through the mixing element, in order to ensure a good mixing. The experimental procedure is the same as described above for single gases under humidified conditions. The mixture of gas used in order to mimic the biogas is composed by 70.0 v/v% of CH_4 and 30.0 v/v% of CO_2, while to mimic the flue gas composition, a mixture of 80.0 v/v% of N_2 and 20.0 v/v% of CO_2 was used. Each experiment was repeated at least twice.

6.3.4 Calibration method

The MS calibration is based on the work of Fraga *et al.* (2017) [148]. A mass spectrometer (Prisma Plus QMG 220 M2, Pfeiffer Vacuum, Germany) was used with an axial beam ion source, emission current 1 mA, electron energy 70eV, single quadrupole, secondary electron multiplier SEM detection. Mass spectrometry identifies and quantifies the target compounds, according to their specific mass to charge ratio (m/z) and intensity of electric signal, providing a characteristic mass spectrum for each specific compound. The calibration was performed using the software Quadera (v4.61) (Pfeiffer Vacuum, Germany), which converts the characteristic intensity (m/z) of each gas (m/z_{N2}=28 and 14, m/z_{CO2}=44 and 28, m/z_{CH4}=15, m/z_{Ar}=40, m/z_{He}=4 and m/z_{H2O}=18), present in the permeate compartment, into volumetric concentration (vol%) or partial pressure.

6.3.5 Calculation methods

The permeation flux of each gas, J_i, based on the flow-rate and molar fraction of standard gas argon, can be calculated, according to Hasegawa *et al.* (2008) [175], as:

$$J_i = \frac{Q_{Ar}}{A} \times \frac{y_i}{y_{Ar}} \qquad \left(\frac{m^3[STP]}{m^2 \cdot s}\right) \tag{2}$$

where Q_{Ar} is the volumetric flowrate of standard gas argon, A is the effective membrane area of permeation (4 cm^2), y_i and y_{Ar} denotes the mole fraction of gas i in the permeate side and the molar fraction of the argon, respectively.

Taking into account that gas permeation is described based on the solution-diffusion model, the permeation flux of gas i is described also as follows [70]:

$$J_i = \frac{P_i}{l}(p_{i0-}p_{il}) \quad (3)$$

where *l* is the membrane thickness, P_i is the gas permeability, p_{io} and p_{il} are the partial pressures of gas i in the feed and the permeate side, respectively.

6.4 Results and discussion

6.4.1 Permeability for pure gases under dry conditions

From the MS results the volumetric concentration of each compound is obtained along time. Using equations 2 and 3, respectively, the flux and permeability of each compound can be calculated. The permeation data for CO_2, is given as an example in Fig. 6.3.

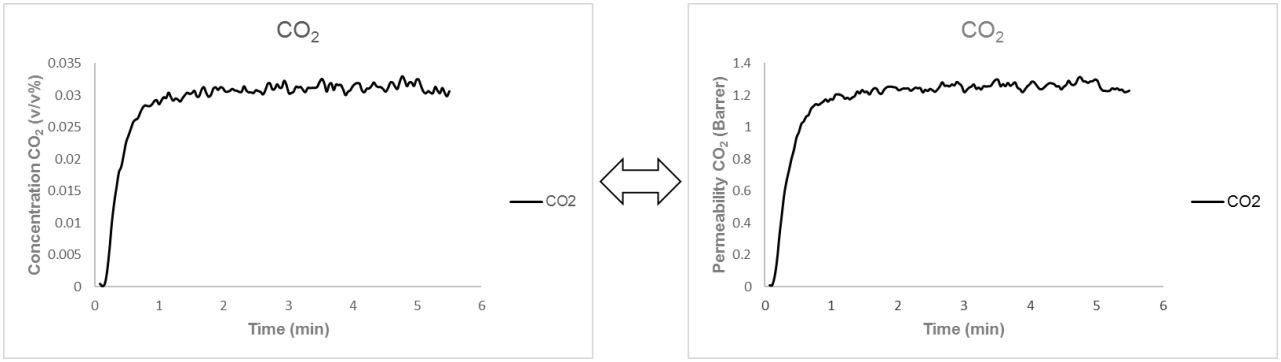


Fig. 6.3: Permeation experiment with dry CO_2: concentration of CO_2 in the permeate when using the FucoPol+GPTMS+$CaCl_2$ membrane, and corresponding permeability, represented against time (T=21 ºC and p_{perm}=70 mbar).

The results of permeability for the various pure dry gases studied are presented in Table 6.1.

Table 6.1: Permeability for dry gases.

Gas	P (barrer)
CO_2	1.33 ± 0.13
N_2	0.17 ± 0.01
CH_4	0.02 ± 0.01

Regarding the results obtained, CO_2 has the highest permeability, 1.33 ± 0.13 barrer, followed by N_2 with a permeability of 0.17 ± 0.01 barrer and CH_4, with a permeability value of 0.02 ± 0.01 barrer. These very low values of permeabilities, in the range of membranes with excellent barrier

properties, were possible to be accurately and reproducibly obtained by mass spectrometry. According to the literature, the low values of gas permeability are characteristic of polysaccharides [160,176] and, in addition, the higher values of carbon dioxide permeability compared with the other gases are characteristic of membranes that present hydrophilic groups [177]. These membranes follow the general behaviour of glassy polymers, where the permeability is controlled by diffusion instead of solubility, which means that the permeability decreases with the increase of the kinetic diameters (3.30 Å for CO_2; 3.64 Å for N_2 and 3.80 Å for CH_4 [178]) of the penetrants (permeability for CO_2>N_2>CH_4) [179].

6.4.2 Permeability for humidified gases – effect of water vapour on the permeability of pure gases

Fig. 6.4 shows the permeability for each gas (CO_2, N_2 and CH_4) against different percentage of the gas humidity content (wt.%) – which corresponds to $g_{H2O}/g_{dry\ gas}$ x 100. The different salts used in the trap (see Fig. 6.2 a)) led to different humidified conditions at the feed compartment measured by the thermohygrometer, in terms of the percentage of the gas humidity content.

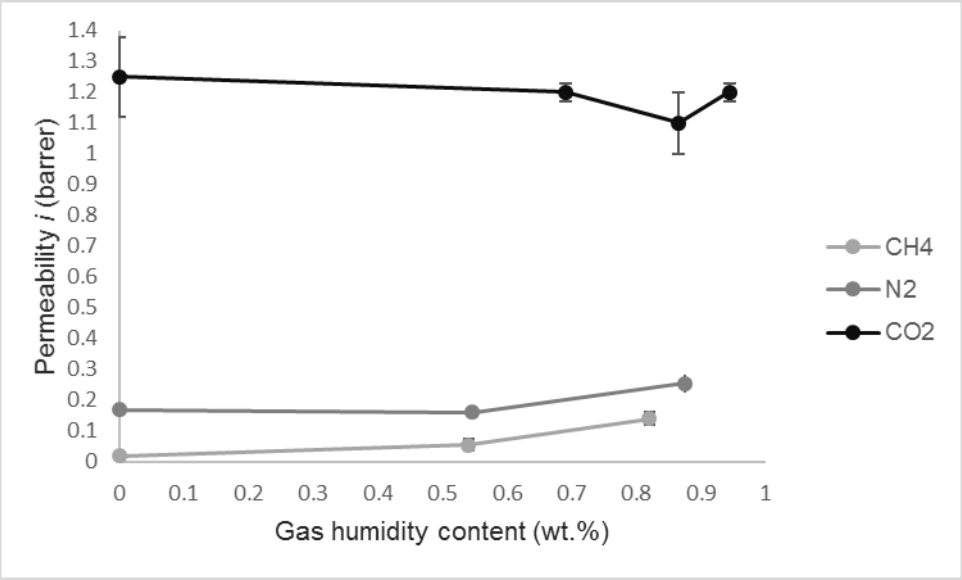


Fig. 6.4: Results for pure gas permeation with different gas humidity content. Note: the error bars in each measurement are, in some cases, smaller than the symbols.

From the results obtained (Fig. 6.4) it is possible to infer that the CO_2 permeability was found to be almost constant, throughout the whole gas humidity content studied. The N_2 permeability was constant below a gas humidity content of 0.55 wt.%, while the CH_4 permeability slightly increased with the increase of water vapour content, in the same conditions. At higher water mass fractions,

the N_2 and CH_4 permeabilities increased dramatically (data not shown), due to plasticisation effects that occur in the membrane, leading to a significant increase of gas permeability [83]. Specifically, in the case of CH_4, the permeability value could not be measured for a 1.20 wt.% humidity content because a sharp increase of permeate pressure was observed and, hence, such a high increase of permeability (higher than 3.2 barrer), strongly suggests a membrane leak. This behaviour may be due to an extremely high extent of membrane swelling and, ultimately, membrane collapse. Similar results were reported by Chen *et al.* (2015) [83] for the permeation of humidified CO_2 and CH_4 through cellulose acetate membranes which, at a water vapour activity of 0.45, suffer from a high swelling effect leading to an exponential increase of CO_2 and CH_4 permeability.

Taking into account the results obtained, it may be concluded that the hybrid polysaccharide membrane is affected by swelling and plasticisation, for gas humidity contents above 0.94 wt.%. Nevertheless, it is also noticed that water vapour affects more the permeability for gases controlled by diffusion (CH_4 and N_2) than the permeability for CO_2, which permeability is mostly controlled by solubility [180]. In the work of Neves *et al.* (2010) [180], it was found a similar behaviour for ionic liquid membranes. The higher permeability for CO_2 when compared to N_2 and CH_4 (see Fig. 6.4) may be explained by the high solubility of this gas in water, when compared with other gases – 34.0, 1.3 and 1.0 mmol/l_{water} at 25.0 ºC, respectively, for CO_2, CH_4 and N_2 [181,182].

The water vapour permeability for different gas humidity content is presented in Fig. 6.5.

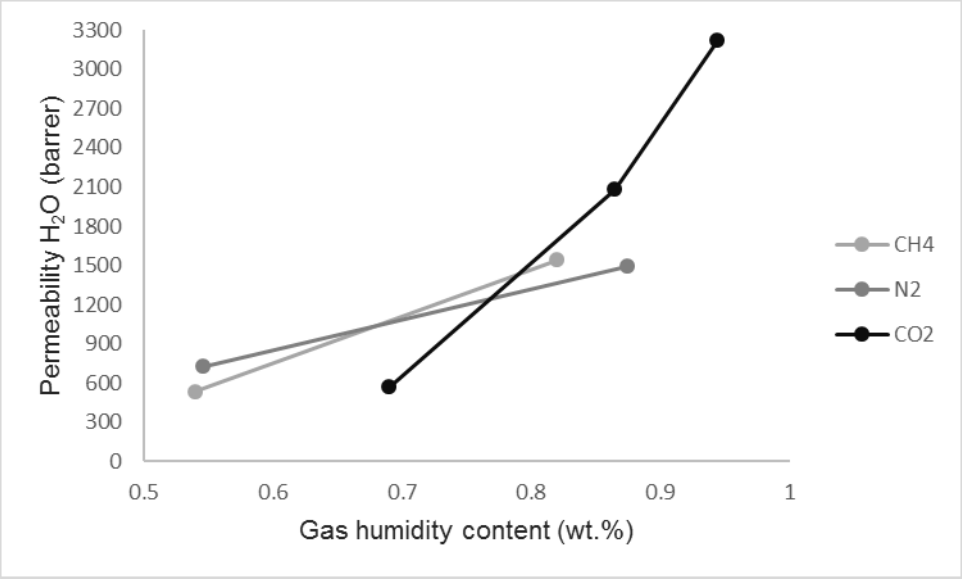


Fig. 6.5: Water permeability for the humidified gases (CO_2, N_2 and CH_4) of the hybrid polysaccharide membrane at 22.0 ºC. Note: the error bars are smaller than the symbols.

Comparing the water vapour permeability values (Fig. 6.5) with the gases' permeability (Fig. 6.4), it can be concluded that this hybrid polysaccharide membrane presents much higher water vapour

permeability values, for all gases studied. These results suggest that this membrane can be considered for gas dehydration due to the high water vapour/gas selectivities.

Analysing the water vapour permeability for the humidified gases under study, it is observed an increase of water vapour permeability with the increase of gas humidity content. This may be related to a plasticisation of the biopolymer, which promotes the increase of solubility of water vapour in the membrane [183] and also its diffusivity. Several studies reported [36,173,83,183,30] the same membrane behaviour with the increase of water content.

The selectivity results of H_2O/gas (CO_2, N_2 and CH_4) for different gas humidity contents are represented in Fig. 6.6.

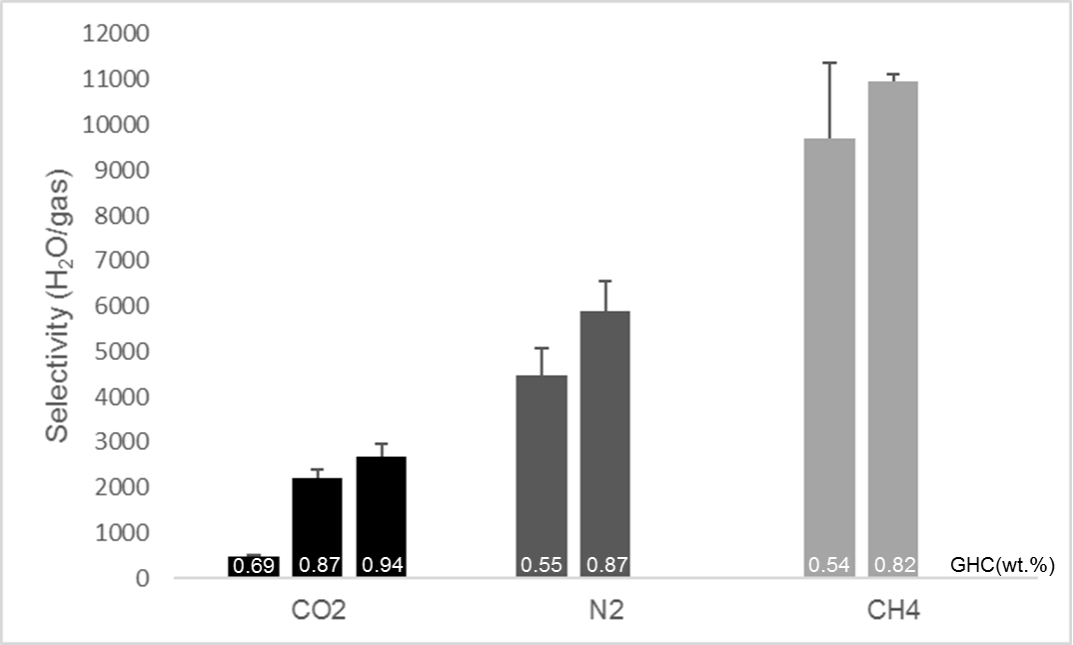


Fig. 6.6: H_2O/gas (CO_2, N_2 and CH_4) selectivity for the dehydration process with the membrane FucoPol+GPTMS 7+$CaCl_2$ at 22.0 ºC. (GHC stands for gas humidity content wt.%).

Comparing the selectivity of water vapour for all gases studied, the selectivity follows the sequence $H_2O/CH_4 > H_2O/N_2 > H_2O/CO_2$ (Fig. 6.6). This occurs due to the very low values of CH_4 permeability compared with N_2 and CO_2 which, despite increasing with the water content, is always lower than 0.2 barrer (until 0.82 wt.% of gas humidity content). As a consequence, a H_2O/CH_4 selectivity of, approximately, 11000 was achieved.

The FucoPol+GPTMS 7+$CaCl_2$ membrane showed high water vapour selectivity values for all gases studied, until a 0.9 wt.% of gas humidity content. For this reason, the gas humidity content chooses to infer about the potential of this hybrid polysaccharide membrane in industrial applications was around this value. In fact, industrial biogas has a water vapour content, at this temperature, of around 1.2 vol.% [184], which is similar to gas humidity content under study (0.8 wt.% of gas humidity in ternary mixture corresponds to 1.0 vol.% of water vapour).

6.4.2.1 Comparison with literature

Most published studies report membrane separation performance for dry and pure gases. However, from a practical point of view, permeation data for gases and water vapour in binary mixtures is required, in order to understand the real interaction between the mixture and the membrane.

A comparison of water vapour permeability and selectivity values for dehydration of various gases in different membranes is given in Table 6.2.

Table 6.2: Comparison of transport performance of different membranes referred in the literature. GHC corresponds to gas humidity content.

Gas	Membrane	Operating Conditions	GHC (wt.%)	a_w	P_{gas} (barrer)	P_{H2O} (barrer)	Sel (H_2O/gas)	Reference
CO_2	TR HAB-6FDA PBO[1]	35 ºC and 4 bar (feed) and 1 bar (perm)	0.35	0.60	358.4	40500	~113	Scholes *et al.* (2014) [185]
	PEO-ran-PPO[2]	50 ºC and 2.5 bar (feed) and 1 bar (perm)	1.35	0.65	598.8	100000	~167	Reijerkerk *et al.* (2011) [30]
	FucoPol+GPTMS+$CaCl_2$	22 ºC and 1.05 bar (feed) and ~70 mbar (perm)	0.69	0.65	1.2	571	482	This work
CH_4	TR HAB-6FDA PBO[1]	35 ºC and 4 bar (feed) and 1 bar (perm)	1.28	0.60	18.0	41000	~2278	Scholes *et al.* (2014) [185]
	CDA[3]	35 ºC and 7.5 bar (feed) and 1 bar (perm)	0.68	0.80	0.2	~22500	~102273	Chen *et al.* (2015) [83]
	FucoPol+GPTMS+$CaCl_2$	22 ºC and 1.05 bar (feed) and	0.82	0.31	0.1(4)	1543	10958	This work

		~70 mbar (perm)						
	PEBAX® 1074	30 ºC and 2.5 bar (feed) and 1 bar (perm)	0.89	>0.8	1.6	50000	~32000	Potreck *et al.* (2009) [173]
N_2	PSf/Si-TFN membrane[4]	30 ºC and 1 bar (feed) and 0.2 bar (perm)	2.13	~0.75	1.8	880	501	Baig *et al.* (2017) [186]
	FucoPol+GPTMS+$CaCl_2$	22 ºC and 1.05 bar (feed) and ~70 mbar (perm)	0.87	0.51	0.3	1494	5891	This work

[1]Polyimide blend films; [2]poly(ethylene oxide) based block copolymers; [3]cellulose diacetate; [4]nanocomposite polysulfone hollow fiber membrane with a thin film with nano-Silicon particles incorporated.

Comparing the transport performance of the hybrid polysaccharide membrane with other membranes reported in the literature (Table 6.2), it is possible to note that the membrane developed in this work is an excellent barrier membrane for all gases studied, presenting gas permeabilities below 1 barrer. Moreover, it is also important to note that this membrane presents, in most cases, a higher selectivity for water. The selectivities obtained for the hybrid polysaccharide membrane are higher or similar to the others referred (with exception of the work of Chen *et al.* (2015) [83] for CH_4 and Potreck *et al.* (2009) [173] for N_2), due to the low values of gas permeability, characteristic of polysaccharides.

According to Baker & Lokhandwala, 2008 [187], for specific applications such as natural gas dehydration, a membrane process cannot lose more than 1% of methane to be economically competitive, when compared with dehydration with glycol. Under these conditions, the use of membranes with very low methane permeabilities, as the hybrid polysaccharide membrane developed in this work, and with a water vapour/methane selectivity ≥ 500 could be an interesting industrial alternative.

6.4.3 Permeability for gas mixtures – Flue gas and biogas dehydration

In order to simulate real industrial applications, a N_2/CO_2 mixed gas with a proportion of 80/20 v/v% and a CH_4/CO_2 mixed gas with a proportion of 70/30 v/v% were prepared to mimic dehydration of flue gas and biogas, respectively. The experiments were carried out under constant humidified conditions, by promoting the contact of these gas streams with the headspace

of a selected saturated solution (which, for the water/air system, has the water activity a_w of 0.52). These results, presented in Table 6.3, were obtained by on-line mass spectrometry as previously described.

The simultaneous determination of the gas(es) permeabilities, as well as water vapour permeability, is very relevant to mimic a real industrial application. Still, similar procedures are rarely described in the literature. In addition, it is important to note that membrane transport performance is related to the difference in gas permeability for the components of the feed mixture, which also depends on many factors, such as kinetic diameter and condensability of penetrant, the free volume of the membrane matrix and gas-polymer interactions [179]. The presence of more than one gas species may affect the individual gas solubility, especially for the most condensable gases, due to the competitive sorption and plasticisation effects, causing a reduction of the membrane transport performance [183,188].

Table 6.3: Transport performance of the hybrid polysaccharide membrane for synthetic flue gas and biogas dehydration.

Mixtures	**Gas humidity content (wt.%)**	**P_{gas} (barrer)***	**P_{CO2} (barrer)**	**P_{H2O} (barrer)**	**Sel (H_2O/CO_2)**	**Sel (H_2O/gas*)**
Flue gas (N_2/CO_2)	0.0	1.6 ± 0.1	0.9 ± 0.0(5)	-	-	
	0.7	1.9 ± 0.0(3)	2.6 ± 0.1	565.0 ± 23.0	218.3 ± 11.6	294.4 ± 12.7
Biogas (CH_4/CO_2)	0.0	0.6 ± 0.0(3)	1.3 ± 0.1	-	-	
	0.8	0.4 ± 0.0(4)	2.0 ± 0.2	1766.3 ± 43.6	888.4 ± 76.9	4041.9 ± 344.0

***gas represents N_2 or CH_4, respectively for flue gas or biogas mixtures

From Table 6.3, it is important to note that the hybrid polysaccharide membrane showed to be effective in flue gas and biogas dehydration (ternary mixtures). Moreover, this membrane presented high water selectivities for the two mixtures analysed, and gas permeabilities were always below 3.0 barrer.

Taking into account the results obtained for the two dry gas mixtures studied, it is possible to see that both mixtures showed similar values for CO_2 permeability relative to pure CO_2 permeability (0.9 barrer and 1.3 barrer, respectively for flue gas and biogas mixture compared to 1.3 in pure CO_2 permeation – see Table 6.1). In contrast, N_2 and CH_4 permeability increased to 1.6 barrer (compared with 0.17 barrer in pure N_2 permeation - Table 6.1) and 0.6 barrer (compared with 0.02 barrer in single gas permeation - Table 6.1).

Due to the plasticisation effect of water, when the mixture of gases is humidified all permeability values increased with exception of CH_4, which decreased (0.6 to 0.4 barrer). This slight decrease

of the absolute value of the CH_4 permeability, in contrast with the high increase of CO_2 permeability in both mixtures (in the presence of water), can be related with the blocking of diffusional pathways by water, which has a higher impact on CH_4 transport than CO_2 due to the larger volume of the CH_4 molecule [183]. This is consistent with the results of other researchers for polyimide membranes [183,189].

Analysing the water permeability, it was found that in the biogas mixture the water permeability is three times higher than the water permeability in the flue gas mixture (see Table 6.3). This result, together with the CH_4 permeability decrease, leads to a H_2O/CH_4 selectivity much higher than the H_2O/N_2 selectivity (4042 and 294, respectively).

The hybrid polysaccharide membranes showed that, in real situations, they have the ability to dehydrate mixtures, due to the low gas permeability characteristic of polysaccharides [160] and also the introduction of inorganic particles in the polymer matrix by the sol-gel technique used, which increases the gas barrier properties of the polymer [190]. In addition, for other relevant industrial dehydrations, such as natural gas (which presents 600-1200 ppm of water vapour [191]), the hybrid polysaccharide membranes may have a high potential, with the advantage of not losing CH_4, due to the low permeability values of these gases.

6.4.4 Membrane Stability

The membrane properties that are important to assure are the permeability for the target solute (water vapour) and for the gas components of the mixture, the selectivity towards the target solute and the membrane stability under operating conditions [179]. To analyse the stability of the membrane, the same membrane was operated during 20 consecutive experiments (during approximately 7 h each experiment, taking into account the purge and testing time-length), with pure and humidified gases. Afterwards, the pure gas permeation experiments of new membranes were compared with “used membranes” in consecutive experiments, after the membrane are exposed to water vapour.

According to Tsvigu *et al.* (2015) [179], glassy polymers, as this membrane, can be influenced by the polymer free volume (that strongly affects the diffusion of small molecules), which is also regulated by the material history (membrane preparation) and the exposure to swelling agents or different thermal treatments. Moreover, when plasticiser gas molecules or vapours, such as CO_2 and water, diffuse through the membrane, the interaction between the penetrants may swell the polymer matrix, increasing the free volume, and, simultaneously, the diffusivity for all gaseous species present.

For CO_2 permeation there was no significant increase in the permeability value. In contrast, the N_2 and CH_4 transport behaviour was slightly different when using a fresh or a repeated used membrane after a total of 7 h of operation in 20 consecutive experiments. Still, it is worth mentioning that, despite increasing, the permeability values for these gases are always lower than

3.0 barrer. This means that the membrane maintains its gas barrier characteristics after long-term exposure to water vapour.

When comparing the water vapour permeation for the fresh and the used membranes, it could be concluded that permeation is rather constant, irrespectively from the gas stream studied. These results are extremely positive and show that the membrane developed keeps its ability for gas dehydration, even after repeated use.

6.5 Conclusions

Hybrid polysaccharide membranes, prepared from a low-cost substrate and developed by a sol-gel method, were evaluated for their potential use in gas dehydration. Two relevant industrial dehydration processes were selected: flue gas and biogas dehydration. In order to mimic real conditions, permeation of pure gases (CO_2, N_2 and CH_4), binary mixtures (CO_2/H_2O, N_2/H_2O and CH_4/H_2O) and ternary mixtures ($80\%N_2/20\%CO_2/H_2O$ and $70\%CH_4/30\%CO_2/H_2O$) were studied at different gas humidity content (% of $g_{H2O}/g_{dry\ gas}$) by on-line mass spectrometry. This technique proved to be a fast, useful and effective tool for gases and water vapour monitoring, even in complex mixtures. The FucoPol+GPTMS+$CaCl_2$ membranes developed revealed to be an excellent gas barrier to all gases studied with permeability values below 1.0 barrer, and presented high selectivity for water vapour transport.

In close-to-real conditions, the hybrid polysaccharide membranes showed the ability to dehydrate gas mixtures (binary and ternary mixtures), with the advantage of not losing gases to the permeate stream, due to their low permeability for the gases studied (CO_2, CH_4 and N_2). This characteristic makes these membranes potential alternatives for other relevant dehydration processes in industry, such as natural gas and air dehydration.

Chapter 7

7 General Conclusions and Future Work

In this PhD thesis two types of microbial exopolysaccharide membranes, made from GalactoPol and from FucoPol, were developed and characterised, in order to study the potential of applying them in industrially relevant dehydration processes: ethanol and gas dehydration. These microbial exopolysaccharides are produced with attractive productivity and polymer yield by fermentation using glycerol as carbon source, a by-product from the biodiesel production. This study examines the potential of using a low cost, abundant by-product to produce membranes, through an environmentally friendly process.

Firstly, GalactoPol membranes were developed by solvent precipitation using acetone and trichloroacetic acid as a crosslinking agent. These membranes are insoluble in aqueous solutions (due to the crosslinking reaction) and resistant to all solvents tested, while maintaining their high affinity for water. Two types of membranes were prepared and compared: homogeneous membranes and composite membranes using polyethersulfone (PES) as support. The composite membranes showed an improved mechanical stability in comparison with the homogeneous membranes, and also a high potential for ethanol dehydration by pervaporation, since a selectivity of 3000 was achieved when processing a feed stream with 5.0 wt.% of water in ethanol. The transport mechanism of water and ethanol through the GaloctoPol membrane was also evaluated noticing that, at lower water content in the feed, transport is dominated by diffusion while, with increasing water content, sorption becomes the controlling mechanism, due to plasticizing effects.

Actually, the purification and extraction of these exopolysaccharides was carried out using sustainable methods (i.e. dia-ultrafiltration), minimizing the use of solvents and their environmental impact.

The influence of two different purification methods, dialysis in a static mode and dia-ultrafiltration in a tangential flow filtration mode was also evaluated. The composite FucoPol membranes prepared, using as active layer the polysaccharide purified by these two methods, were compared in terms of structure, resistance to solvents, mechanical properties and transport performance for ethanol dehydration by pervaporation. Both composite membranes exhibited identical resistance to organic solvents, but presented significant differences in terms of swelling degree and transport selectivity. The membranes developed using the polysaccharide purified by dia-ultrafiltration revealed to be more adequate for ethanol dehydration, since a water/ethanol selectivity of 143 for a feed composition of 10.0 wt.% water in ethanol was achieved. The membrane forming solution obtained by dia-ultrafiltration showed a higher apparent viscosity and the presence of smaller polysaccharide aggregates, due to the shear stress caused by pumping and recirculation imposed in the dia-ultrafiltration process, when compared to the membrane forming solution of dialysed

polysaccharide. It was found that the shear stress conditions imposed during dia-ultrafiltration induce a better dispersion of the polymer chains in solution, leading to a tighter membrane, with a better transport performance.

In order to improve the long-term stability of the FucoPol membranes, novel hybrid membranes were prepared, combining the best properties of the inorganic network with the selectivity of the microbial polysaccharides. These membranes were applied in pervaporation processes for ethanol dehydration, as well as in gas dehumidification. A sol-gel reaction using (3-Glycidyloxypropyl) trimethoxysilane (GPTMS) as silica precursor was carried out to develop the hybrid polysaccharide membranes. It was shown an improvement of the thermal and mechanical properties of the hybrid membranes, when compared with GalactoPol and FucoPol membranes. In addition, these membranes presented a water selectivity for ethanol dehydration very similar to the values obtained for the commercial membrane PERVAP® 4101. However, when the membranes were exposed to solvent media containing water for long-term operation periods (3 days) they became progressively unstable. In contrast, experiments with hybrid FucoPol membranes for N_2 dehydration revealed a good reproducibility and stability during 18 hours, which allow us to foresee them as potential candidates for gas dehydration processes.

Considering this result, the potential use of hybrid FucoPol membranes for gas dehydration was evaluated, using an on-line monitoring mass spectrometry (MS) technique to characterise gas transport in real-time during the whole permeation process. In order to mimic real industrial applications – flue gas and biogas dehydration – the permeation of water vapour and pure gases (CO_2, CH_4 and N_2) with different conditions of relative humidity, and also gas mixtures (20 vol.% CO_2 + 80 vol.% N_2 and 70 vol.% CH_4 + 30 vol.% CO_2) were monitored. The membranes developed revealed to be excellent barriers to all gases studied with permeability values below 1.0 barrer, and presented high water vapour selectivity. Under close-to-real situations, these membranes showed stability (for at least 140 h) and the ability to dehydrate mixtures, with the advantage of not losing N_2 or CH_4, to the permeate stream, due to the low permeability values of these gases. Moreover, it was proved that the mass spectrometry technique is a versatile and efficient monitoring tool, able to follow on-line and in real-time, both the transient and the steady state period of the permeation process.

The microbial polysaccharide membranes developed during this PhD work have shown to be able to dehydrate ethanol and gases, under close-to-real conditions, with high water selectivities. In addition, it was found that the sol-gel crosslinking protocol used improved the transport performance and mechanical properties of the membranes developed, in order to fit to the proposed industrial applications.

7.1 Suggestions for future work

The main goal of this work is the development and characterisation of microbial exopolysaccharide membranes, obtained from a low cost substrate, in dehydration processes. The high affinity to water, resistance of solvents and barrier properties, make them particularly interesting to be applied in solvent dehydration, as well as in gas dehydration. However, considering the knowledge acquired during this work, it was found that the crosslinking agent and the protocol used for membrane synthesis are the determining factors to assure adequate mechanical and transport properties, as well as operating stability. The protocol for membrane synthesis can be improved and extended in different ways. The following recommendations are proposed:

- In order to improve the stability of the FucoPol membranes in organic solvents containing water, other silica precursors such as tetraethylorthosilicate (TEOS), can be also incorporated in the polymeric matrix together with GPTMS, in order to minimize the swelling of the membranes [192,193]. This procedure should be applied to guarantee the total crosslinking reaction between the inorganic particles and the polymeric matrix, in order to avoid the use of a posterior crosslinking reaction with calcium, which is possibly being leached during the long exposure to ethanol/water solutions.
- The incorporation of graphene oxide will be an interesting choice to develop water-selective membranes with outstanding mechanical stability and physicochemical properties [194].
- Two alternative techniques should be tested and optimised in order to obtain thinner and uniform active layers, when preparing composite membranes: spin coating [133] and spry coating [195]. The purpose is to increase the flux while maintaining a high selectivity.
- Further work should be performed for the dehydration of other relevant organic solvents, namely acetic acid. The dehydration of acetic acid represents a challenge for common membranes, since the acidity can damage the polymeric matrix over time. During preliminary experiments, the FucoPol membrane has proved to be resistant to acidic conditions, being a potential alternative for this purpose.
- In order to quantify the membrane changes due to swelling, and predict the transport performance across the membrane it will be important to measure the free volume of the membranes developed. Positron annihilation lifetime spectroscopy (PALS) is one of the most powerful techniques to determine free volume size and free volume fractions in polymeric materials [196,197]. Studies with PALS are, therefore, recommended.

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